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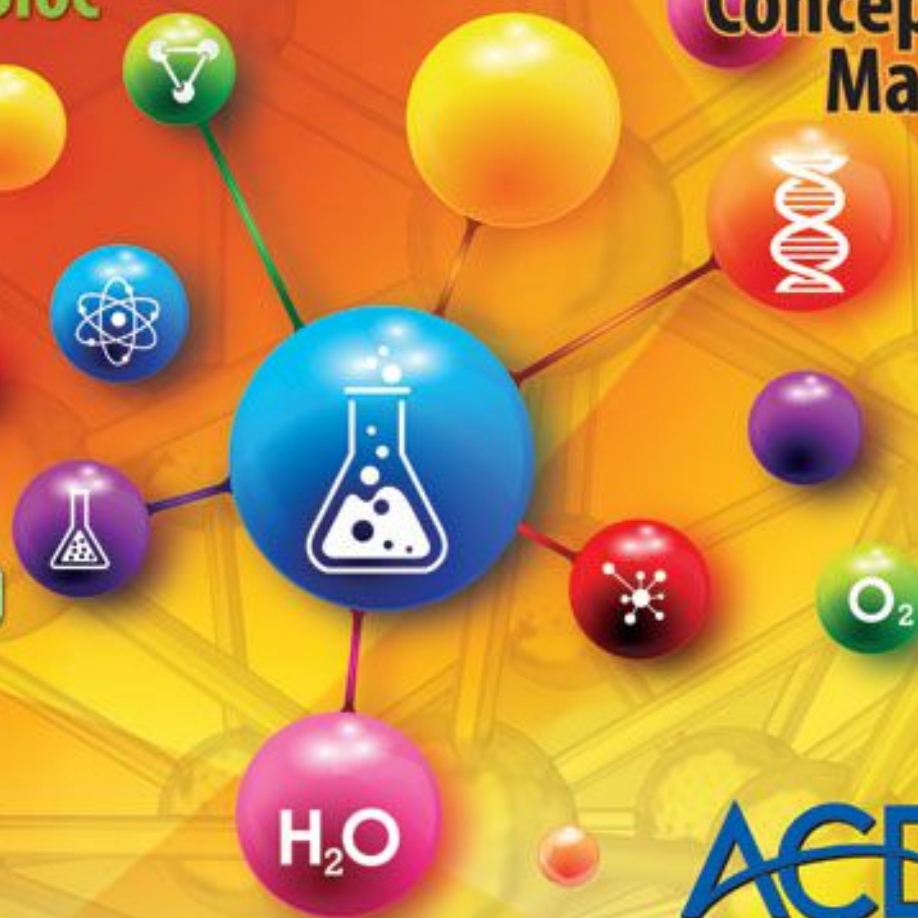
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CHEMISTRY today

Volume 24

No. 12

December 2015

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Payments should be made directly to : MTG Learning Media (P) Ltd,
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CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

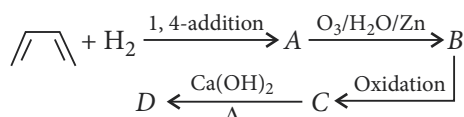
We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 29

JEE MAIN/PMTs

- Ratio of the rates of diffusion of He and H_2 at $0^\circ C$ is same to the case
 - when temperature is changed to $100^\circ C$
 - when O_2 and CH_4 are taken instead of He and H_2 respectively
 - when volume of the flask is doubled
 - when CH_4 and O_2 are taken instead of He and H_2 respectively.
 - I and II
 - II and III
 - I, II and III
 - I and IV

- Study the given sequence of reactions :



If 'D' is an ozonolysis product of 'E' then 'E' is

- -
 -
 -
- Which reaction yields the greatest quantity of chlorine from a given quantity of hydrochloric acid?
 - Warming conc. HCl with MnO_2
 - Warming conc. HCl with Pb_3O_4
 - Mixing conc. HCl with $KMnO_4$
 - Treating bleaching powder with HCl

- A weak monobasic acid is titrated against NaOH. After the addition of 20 mL and 40 mL of NaOH the

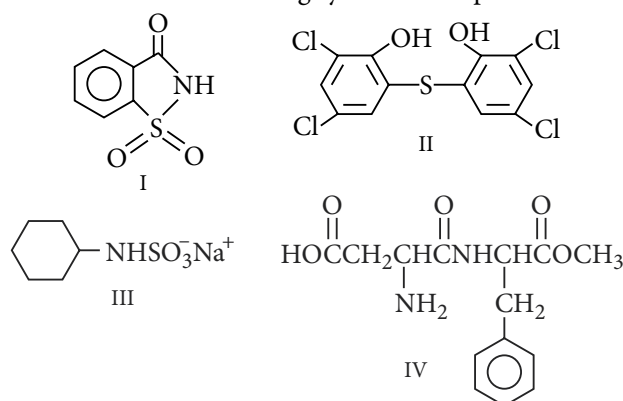
pH of solutions are 4 and 5 respectively. The volume of NaOH required to reach equivalence point is

- 35 mL
 - 3.5 mL
 - 45 mL
 - 40 mL
- Study the given sequence of reactions,

$$\begin{array}{l} A + NaOH \xrightarrow{\Delta} B \xrightarrow{HCl} \text{White fumes} \\ \text{Colourless salt} \\ \downarrow CaCl_2 \\ C \xrightarrow{KMnO_4(\text{acid})} \text{Colourless} \\ \text{White ppt.} \end{array}$$
 A, B and C are respectively
 - Al_2O_3 , NH_3 and $H_2C_2O_4$
 - $(NH_4)_2C_2O_4$, NH_3 and CaC_2O_4
 - NH_4OH , $H_2C_2O_4$, CaC_2O_4
 - none of these.

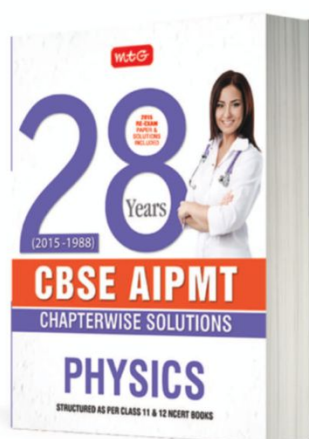
JEE ADVANCED

- Consider the following synthetic compounds :

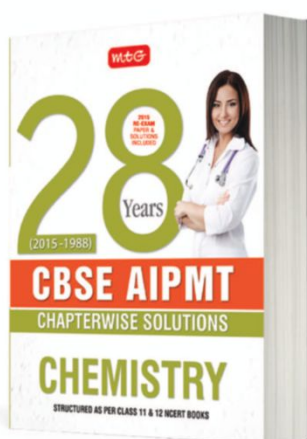


Which of the above compounds are used as sweetening agents?

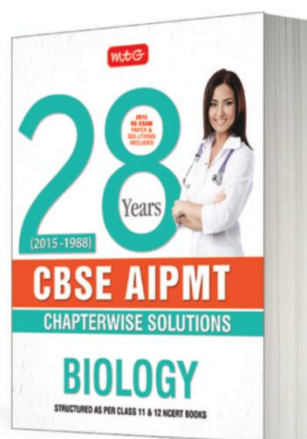
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HIGHLIGHTS:

- Chapterwise questions of last 28 years' (2015-1988) of CBSE-PMT
- Chapterwise segregation of questions to help you assess the level of effort required to succeed
- An unmatched question bank series with close to 1,000 pages having detailed solutions by experts



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- (a) I, III and IV (b) II, III and IV
(c) I, II and IV (d) All of these

COMPREHENSION

Faraday's first law of electrolysis : The mass of a substance liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte. Quantity of electricity refers to the quantity of electrical charge, typically measured in coulomb.

Faraday's second law of electrolysis : When the same quantity of electricity is passed through different electrolytes connected in series, the masses of the substances produced at the electrodes are directly proportional to their equivalent weights.

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

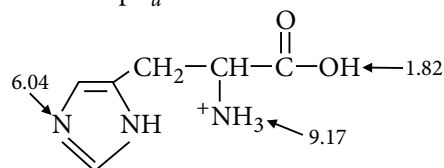
7. The volume of gases evolved by passing 0.965 A current for 1 hour through an aqueous solution of CH_3COONa at 25°C and 1 atm is

- (a) 2.762 L (b) 1.762 L
(c) 17.62 L (d) none of these.

8. If three faradays of electricity is passed through the solutions of AgNO_3 , CuSO_4 and AuCl_3 , the molar ratio of the cations deposited at the cathode is
(a) 1 : 1 : 1 (b) 1 : 2 : 3
(c) 3 : 2 : 1 (d) 6 : 3 : 2

INTEGER VALUE

9. Number of σ bonds present in the molecule of tetracyanoethylene is
10. Histidine has pK_a values as indicated



At $\text{pH} = 8$, the total number of nitrogen atoms which exist in protonated form is



CBSE Scraps Problem Solving Assessment Test for Std. IX, XI

Mid-way through the academic year, the Central Board of Secondary Education (CBSE) on 30 October, 2015 decided to do away with the Problem Solving Assessment (PSA) test from the 2015-2016 academic year. The assessment began in 2013 for students of classes IX and XI, who were expected to solve application-based problems to hone their research and analytical skills.

Ever since the PSA was introduced, it was resented by faculty members and students, who cited its ambiguous nature of the assessment, particularly students inclined towards humanities and social sciences subjects. The test aimed to help students assess their ability to comprehend and process information and did not merely assess the subject matter.

On 30 October, 2015 afternoon, to the surprise of CBSE school principals, an e-mail came from the regional office, intimating them of the PSA being dropped with immediate effect. K.K. Choudhury, Controller of Examination, in his communication to school principals, said

that the board has "decided to do away with the conduct of PSA in classes IX and XI from the session 2015-2016".

Students who were unable to attend the PSA in class IX and scored poor marks were allowed to take up a formative assessment test in class X. 30 October, 2015 circular issued by the board, however, asks school to conduct a formative assessment for students who were in class IX in 2014-2015 academic year and could not attend the PSA or want to improve their scores.

While a section of teachers welcomed the move, saying that there was a lot of "ambiguity" and it was a hard assessment to crack, a teacher of the Bengaluru-based school, however, said that this was a "good experiment" of the board that failed since it did not have clear cut directions.

Deepa Sridhar, principal, Sri Kumaran's Children's Home, Bengaluru, said that she was not happy with the move as she felt that it was a good method for students to analyse their aptitude. "Particularly in the light of emphasis given to the Continuous and Comprehensive Evaluation method,

assessments like the PSA would help children as well as us gauge their aptitude," she said.

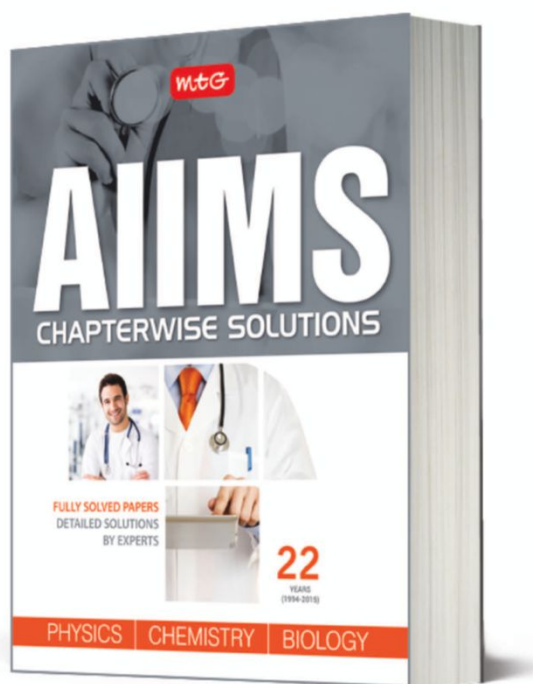
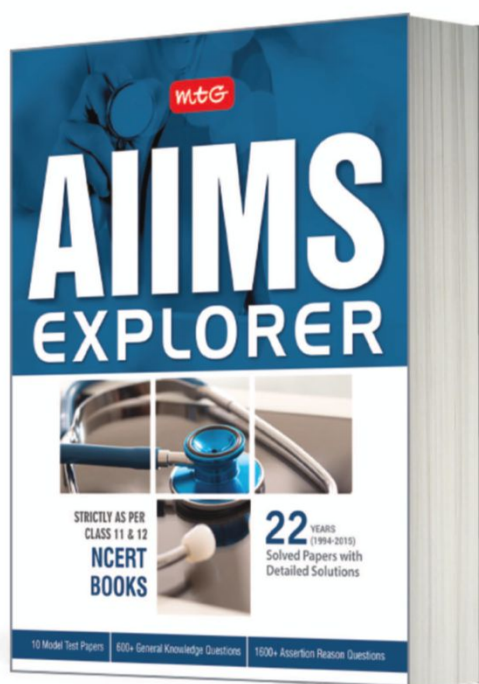
What PSA is all about

One of the objectives of the assessment was to help students analyse life situations, comprehend and interpret it. The test assesses three aspects such as language convention, qualitative reasoning and quantitative reasoning. Problem Solving Assessment (PSA) score is 10 per cent of total assessment for class IX for one language, mathematics, science and social science for class IX students. In class IX, students had three formative assessment, one PSA and two summative assessment. For class XI, students were issued separate certificate for the assessment. Once the students go to class X and XII (who appeared for PSA when they were in IX and XI) they are given the option to improve their PSA score. It consists of 60 multiple choice questions that carry 60 marks.

Courtesy : The Hindu



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HIGHLIGHTS:

- 22 years' (1994-2015) Solved Papers with Detailed Solutions
- 10 Model Test Papers
- 600+ General Knowledge Questions
- 1600+ Assertion Reason Questions
- 22 years' (1994-2015) Chapterwise Solutions
- Subjectwise distribution of 22 years' questions

PRACTICE PAPER

PMT

CLASS
XI

SINGLE OPTION CORRECT

This paper contains 45 **multiple choice questions**. Each question has four choices (a), (b), (c) and (d), out of which **ONLY ONE** is correct. (Mark only One Choice).

Marks : $45 \times 4 = 180$

Negative Marking (–1)

1. The total spin resulting from a d^7 configuration is
(a) $3/2$ (b) $1/2$
(c) 2 (d) 1

2. A certain particle carries 2.5×10^{-16} C of static electric charge. Calculate the number of electrons present in it.
(a) 1563 (b) 15630
(c) 3021 (d) 2345

3. The quantum numbers of four electrons are given below :

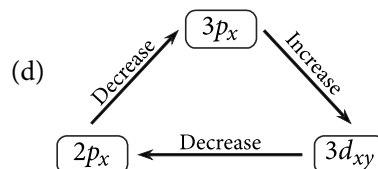
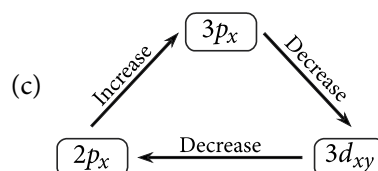
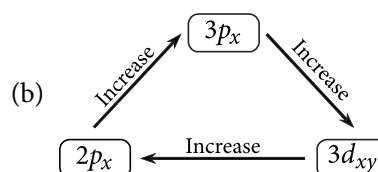
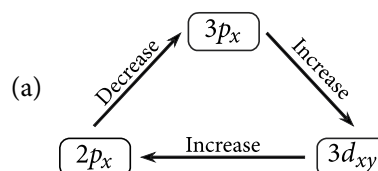
	n	l	m	s
(1) Electron 1	3	0	0	$-1/2$
(2) Electron 2	4	0	1	$1/2$
(3) Electron 3	3	2	0	$1/2$
(4) Electron 4	3	1	0	$-1/2$

The correct order of decreasing energy of these electrons is

- (a) Electron 3 > Electron 1 > Electron 4 > Electron 2
(b) Electron 4 > Electron 2 > Electron 3 > Electron 1
(c) Electron 3 > Electron 2 > Electron 4 > Electron 1
(d) Electron 2 > Electron 4 > Electron 3 > Electron 1
4. $\frac{1}{4}$ th of Avogadro number of atoms of an element absorb energy 'X' kJ for ionisation, the ionisation energy of one atom of the element is

- (a) $\frac{2X}{N_0}$ (b) $\frac{4X}{N_0}$
(c) $\frac{4N_0}{X}$ (d) $\frac{N_0}{X}$

5. Which of the following is correct about energy?



6. The following subshells are involved for 6th period elements in periodic table except
(a) 4f (b) 5d
(c) 6s (d) 5p

Contributed by **Dr. Sangeeta Khanna**, Chemistry Coaching Circle, Chandigarh, 09814129205

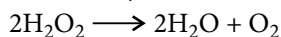
7. From the given set of species, point out the species from each set having the least atomic radius :

(P) O^{2-} , F^- , Na^+ (Q) Cu, Zn, Na
(R) Li, Be, Mg (S) He, Li^+ , H^-

Correct answer is

(a) O^{2-} , Cu, Li, H^- (b) Na^+ , Cu, Be, Li^+
(c) F^- , Zn, Mg, He (d) Na^+ , Cu, Be, He

8. In the reaction,

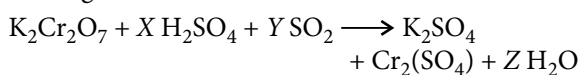


(a) oxygen is oxidised only
(b) oxygen is reduced only
(c) oxygen is neither oxidised nor reduced
(d) oxygen is both oxidised and reduced.

9. What is the maximum number of orbitals that can be identified with the following quantum number $n = 3$, $l = 1$, $m_l = 0$?

(a) 4 (b) 1 (c) 2 (d) 3

10. In the given reaction,



X, Y, Z are

(a) 1, 3, 1 (b) 4, 1, 4 (c) 3, 2, 3 (d) 2, 1, 2

11. 20 cm^3 of a gaseous hydrocarbon was mixed with 150 cm^3 of oxygen. The mixture was sparked so that the hydrocarbon was completely burnt. The gaseous products had a total volume of 130 cm^3 . When this product was passed over soda lime, the volume of the product decreases to 90 cm^3 . All gases were measured at S.T.P. Deduce the molecular formula of the hydrocarbon.

(a) C_2H_4 (b) CH_4 (c) C_2H_2 (d) C_2H_6

12. In which one of the following pairs of the species are isoelectronic as well as isotopic? (At. no. of Ca = 20, Ar = 18, K = 19, Mg = 12, Fe = 26, Na = 11)

(a) $^{40}Ca^{+2}$, ^{40}Ar (b) $^{39}K^+$, $^{40}K^+$
(c) $^{24}Mg^{+2}$, ^{25}Mg (d) ^{23}Na , $^{24}Na^+$

13. Which of the following contains maximum number of particles?

(a) 1 kg electron
(b) 10^5 mg neutron
(c) 1 kg proton
(d) 1000 g hydrogen atom

14. Identify the incorrect statement(s).

I. The maximum probability of finding electron in the $d_{x^2-y^2}$ orbital is at an angle of 45° from x and y-axes.

II. Each f-orbital has a total of four nodes.

III. At same velocity a neutron has lesser wave nature than an electron.

(a) I and II (b) II and III
(c) I and III (d) All of these

15. Reason of lanthanoid contraction is

(a) decreasing screening effect
(b) negligible screening effect of 'f' orbitals
(c) increasing nuclear charge
(d) decreasing nuclear charge.

16. For a hydrogen atom, which electronic transition would result in the emission of a photon with the highest energy?

(a) $5f \longrightarrow 3d$ (b) $4p \longrightarrow 2s$
(c) $3p \longrightarrow 6d$ (d) $2s \longrightarrow 3p$

17. The masses of photons corresponding to the first lines of the Lyman and the Balmer series of the atomic spectrum of hydrogen are in the ratio of

(a) 4 : 9 (b) 27 : 5 (c) 9 : 4 (d) 1 : 1

18. 0.25 g of an element 'M' react with excess of fluorine to produce 0.547 g of MF_6 . Approximate atomic mass of M is [At. mass of F = 19]

(a) 52 (b) 95 (c) 32 (d) 206

19. A metallic oxide contains 40% oxygen. How many electrons will be present in valence shell of metal if its atomic mass is 24?

(a) 3 (b) 2 (c) 1 (d) 4

20. What will be the four quantum numbers of last electron of Sc - 21?

(a) $n = 4$; $l = 0$; $m = 0$; $s = +\frac{1}{2}$
(b) $n = 3$; $l = 2$; $m = 0$; $s = +\frac{1}{2}$
(c) $n = 4$; $l = 1$; $m = 0$; $s = +\frac{1}{2}$
(d) $n = 3$; $l = 3$; $m = 0$; $s = +\frac{1}{2}$

21. The angular momentum of 3p-orbitals in terms of \hbar $\left\{ \hbar = \frac{h}{2\pi} \right\}$ is

(a) $\sqrt{2}\hbar$ (b) $2\hbar$
(c) $\frac{\hbar}{\sqrt{2}}$ (d) $\frac{\hbar}{2\pi}$

22. How many of the following will have four unpaired electrons? [At. no. : Co = 27; Fe = 26; Sc = 21; Cu = 29; Cr = 24; Mn = 25]

Fe, Fe^{+2} , Mn^{+2} , Mn^{+3} , Cu^{+2} , Sc^{+3} , Cr^{+2} , Nitrogen, Co^{+3}
(a) 5 (b) 3 (c) 2 (d) 6

23. The atomic masses of He and Ne are 4 and 20 a.m.u respectively. The value of the de Broglie wavelength of He gas at 200 K is 'M' times that of the de Broglie wavelength of Ne at 1000 K. 'M' is
(a) 5 (b) 4 (c) 3 (d) 2
24. The atomic numbers of elements X, Y, Z are 19, 21 and 25 respectively. The number of electrons present in the 'M' shells of these elements follow the order
(a) $Z > Y > X$ (b) $X > Y > Z$
(c) $Z > X > Y$ (d) $Y > Z > X$
25. Which of the following statements is correct?
(a) Oxidation state of carbon in C_3O_2 is $+\frac{2}{3}$.
(b) Oxidation state of oxygen in ozone is -2.
(c) Oxidation state of oxygen in potassium superoxide is $+\frac{1}{2}$.
(d) Oxidation states of nitrogen in ammonium nitrate are -3 and +5.
26. In which of the following changes both the electrons are removed from same orbital?
(a) $Cu \longrightarrow Cu^{2+} + 2e^-$
(b) $Cr \longrightarrow Cr^{2+} + 2e^-$
(c) $Ge \longrightarrow Ge^{2+} + 2e^-$
(d) $Zn \longrightarrow Zn^{2+} + 2e^-$
27. The chemistry of lithium is very similar to that of magnesium even though they are placed in different groups. Its reason is that
(a) both are found together in nature
(b) both have nearly the same size
(c) both have similar electronic configuration
(d) the ratio of their charge to size is nearly the same.
28. Which of the following does not have three significant figures?
(a) 6.02×10^{23} (b) 0.25
(c) 6.60×10^{-34} (d) 1.50
29. In which of the following first ion or element is less electronegative?
(a) F and Cl (b) Fe^{+3} and Fe^{+2}
(c) O and N (d) S and N
30. Which of the following elements will have highest 3rd ionisation energy?
(a) Be (b) Mg (c) Fe (d) Mn
31. Electron affinity of 2nd period element is less than 3rd period elements of p-Block due to
(a) less effective nuclear charge
(b) more repulsion between valence electron and added electron
(c) absence of d-orbitals is 2nd shell
(d) 2nd period elements cannot expand their octet.
32. Which of the following is correct order of conductance of ions in aqueous solution?
(a) $Li^+_{(aq.)} > Na^+_{(aq.)} > K^+_{(aq.)} > Rb^+_{(aq.)} > Cs^+_{(aq.)}$
(b) $Li^+_{(aq.)} < Na^+_{(aq.)} < K^+_{(aq.)} < Rb^+_{(aq.)} < Cs^+_{(aq.)}$
(c) $Li^+_{(aq.)} < K^+_{(aq.)} < Na^+_{(aq.)} < Rb^+_{(aq.)} < Cs^+_{(aq.)}$
(d) None of these
33. Which of the following elements has three outermost incomplete shells?
(a) Kr (36) (b) I (53)
(c) La (57) (d) Ga (31)
34. A non-radioactive element is paramagnetic and also form coloured paramagnetic compounds which can act as a catalyst. This element will be placed preferably in which block of periodic table?
(a) s-Block (b) p-Block
(c) d-Block (d) f-Block
35. Which of the following compounds will have maximum covalent character?
(a) AgF (b) AgCl (c) AgI (d) AgBr
36. What is the mass of the precipitate formed when 8.45 g solution of $AgNO_3$ is mixed with 2.9 g NaCl solution? [Mol. wt. of $AgNO_3$ = 170; Mol. wt. of NaCl = 58.5; Mol. wt. of AgCl = 143.5]
(a) 7 g (b) 14 g (c) 28 g (d) 3.5 g
37. What is the mole fraction of the solute in a 1.00 m aqueous solution?
(a) 0.0354 (b) 0.0177 (c) 0.177 (d) 1.770
38. Which is the correct order of increasing energy of the listed orbitals in the atom of titanium? (At. no. Z = 22)
(a) 3s 3p 3d 4s (b) 3s 3p 4s 3d
(c) 3s 4s 3p 3d (d) 4s 3s 3p 3d
39. 0.24 mol of a magnesium carbonate sample decomposes on heating to give carbon dioxide and 8.0 g magnesium oxide. What will be the percentage purity of magnesium carbonate in the sample? (At. wt. : Mg = 24)
(a) 60 (b) 83 (c) 75 (d) 96
40. The number of water molecules is maximum in
(a) 18 gram of water
(b) 18 moles of water
(c) 18 molecules of water
(d) 1.8 gram of water.

ASSERTION & REASON

In this type of questions, a statement of assertion (A) is followed by a statement of reason (R). Mark the correct choice as :

- If A and R both are correct and R is the correct explanation of A.
- If A and R both are correct but R is not the correct explanation of A.
- A is true but R is false.
- A is false but R is true.

41. **Assertion :** The ψ_{640} represents an orbital.

Reason : The orbital will be 6f.

42. **Assertion :** Decomposition of CaCO_3 is an intramolecular redox reaction.

Reason : Number of electrons lost by one element is equal to number of electrons gained by another of the same molecule in intramolecular redox.

43. **Assertion :** If specific heat of a metal is given, its approximate atomic mass can be calculated.

Reason : According to Dulong and Petit's law, approximate atomic mass of metal = $\frac{6.4}{\text{Specific heat}}$

44. **Assertion :** α -rays possess maximum ionizing power.

Reason : Kinetic energy of α -particles in α -rays is maximum among three types of radiations.

45. **Assertion :** Fe^{2+} has 24 electrons hence, its electronic configuration is similar to that of Cr(24): $[\text{Ar}]3d^5 4s^1$.

Reason : All the five unpaired electrons in 3d gives stability to the ion.

SOLUTIONS

1. (a) : For d^7 , three unpaired electrons,

$$\text{spin} = 3 \times \frac{1}{2} = \frac{3}{2}$$

2. (a) : Charge on particle = $2.5 \times 10^{-16} \text{ C}$

We know, charge on an electron = $1.6 \times 10^{-19} \text{ C}$

$$\text{So, no. of electrons in the particle} = \frac{2.5 \times 10^{-16} \text{ C}}{1.6 \times 10^{-19} \text{ C}}$$

3. (c) : The correct order of decreasing energy will be : electron 3 which has higher energy than 2 and in the given order.

4. (b) : $\frac{1}{4} N_0$ (i.e., $\frac{1}{4}$ mole) atoms require energy = X kJ

$1 N_0$ (i.e., 1 mole) atoms require energy = 4X kJ

$$1 \text{ atom requires energy} = \frac{4X}{N_0} \text{ kJ}$$

5. (b)

6. (d) : 5p is filled in 5th period.

7. (b) : (P) $\text{O}^{2-} > \text{F}^- > \text{Na}^+$

(Q) $\text{Cu} < \text{Zn} < \text{Na}$

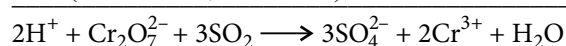
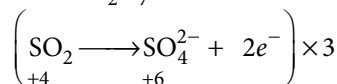
(R) $\text{Mg} > \text{Li} > \text{Be}$ or $\text{Li} > \text{Be} < \text{Mg}$

(S) $\text{H}^- > \text{He} > \text{Li}^+$

8. (d)

9. (b)

10. (a) : $6e^- + \text{Cr}_2\text{O}_7^{2-} \longrightarrow 2\text{Cr}^{3+}$



11. (a) : $\text{C}_x\text{H}_y + \left(x + \frac{y}{4}\right) \text{O}_2 \longrightarrow x\text{CO}_2 + \frac{y}{2} \text{H}_2\text{O}$

$$20 \quad 20 \left(x + \frac{y}{4}\right) \quad 20x = 40$$

$$x = 2$$

Oxygen gas used = $150 - 90 = 60$

$$20 \left(2 + \frac{y}{4}\right) = 60 \Rightarrow y = 4$$

12. (b) : The species which contain same number of electrons as well as same atomic number (Z), is known as isoelectronic and isotopic.

	$^{39}\text{K}^+$	$^{40}\text{K}^+$
Atomic no.	19	19
Total electrons	18	18

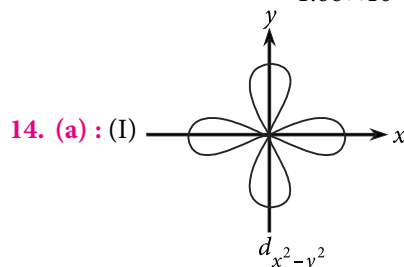
13. (a) :

$$\text{Number of electrons} = \frac{1}{9.1 \times 10^{-31}} = \frac{10^{31}}{9.1} = 1.1 \times 10^{30}$$

$$\text{Number of protons} = \frac{1}{1.66 \times 10^{-24}} = 6.02 \times 10^{23}$$

$$\text{Number of neutrons} = \frac{10^5 \times 10^{-6}}{1.67 \times 10^{-24}} = 5.98 \times 10^{22}$$

$$\text{Number of H-atoms} = \frac{1000 \times 10^{-3}}{1.66 \times 10^{-24}} = 6.02 \times 10^{23}$$



(II) angular node = l and total node = n - 1

(III) due to more mass

15. (b)

16. (b): 2 - 3 is absorption of energy
4 - 2 is emission of energy

17. (b): $\Delta E = mc^2$

For Lyman series, $m_1 c^2 \propto (1/1^2 - 1/2^2) \propto \frac{3}{4}$

For Balmer series, $m_2 c^2 \propto (1/2^2 - 1/3^2) \propto \frac{5}{36}$

$m_1/m_2 = (3 \times 36)/(4 \times 5)$

$m_1 : m_2 = 27 : 5$

18. (b): $M + 3F_2 \longrightarrow MF_6$

Number of gram equivalents of M = Number of
gram equivalents of MF_6

$$\frac{0.25}{E} = \frac{0.547}{E + 19} \text{ (where, } E = \text{Eq. weight of } M)$$

$$E \times 0.25 + 4.75 = 0.547E$$

$$4.75 = 0.547E - 0.25E \Rightarrow E = 15.8$$

Eq. wt. \times valency = At. wt

$$15.8 \times 6 = \text{At. wt.}$$

$$94.8 = \text{At. wt.}$$

19. (b): Eq. mass = 12; Valency = $\frac{24}{12} = 2$

20. (b)

21. (a): Angular momentum in an orbital

$$= \sqrt{\ell(\ell+1)} \cdot \frac{h}{2\pi}$$

$$= \sqrt{1(1+1)} \cdot \frac{h}{2\pi} = \sqrt{2} \times \hbar$$

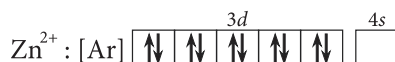
22. (a): Fe, Fe^{+2} , Mn^{+3} , Cr^{+2} , Co^{+3}

$$23. (a): \frac{\lambda_{He}}{\lambda_{Ne}} = \sqrt{\frac{M_{Ne}}{M_{He}} \cdot \frac{K.E_{Ne}}{K.E_{He}}} = \sqrt{\frac{M_{Ne}}{M_{He}} \cdot \frac{T_{Ne}}{T_{He}}}$$

$$= \sqrt{\frac{20}{4} \times \frac{1000}{200}} = 5$$

24. (a): As Z has 13 electrons, Y has 9 electrons and X has 8 electrons in M shell.

25. (d)



Both the electrons are removed from same orbital 4s.

27. (d): Similarity between Li and Mg is called diagonal similarity.

Li^+ and Mg^{2+} have similar ratio of charge to size (ϕ).

28. (b)

29. (d)

30. (a)

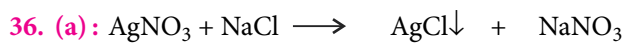
31. (b)

32. (b)

33. (c)

34. (c)

35. (c)



$$\text{Initial } \frac{8.45}{170}$$

$$\frac{2.9}{58.5}$$

$$0$$

$$0$$

$$= 0.049 \text{ mol}$$

$$= 0.049 \text{ mol}$$

$$\text{After } 0$$

$$0$$

$$0.049 \text{ mol}$$

$$0.049 \text{ mol}$$

reaction

$$\text{Mass of } AgCl \text{ precipitated} = 0.049 \times 143.5 \text{ g} = 7 \text{ g}$$

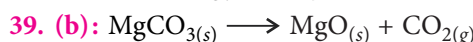
37. (b): 1.00 m solution means 1 mole solute is present in 1000 g water.

$$n_{H_2O} = \frac{1000}{18} = 55.5 \text{ mol}$$

$$x_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{H_2O}} = \frac{1}{1 + 55.5} = 0.0177$$

38. (b): $Ti(22) : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$

Order of energy is 3s 3p 4s 3d



Moles of $MgCO_3 = 0.24 \text{ mol}$

From above equation,

1 mole $MgCO_3$ gives 1 mole MgO

\therefore 0.24 mole $MgCO_3$ will give 0.24 mole MgO

$$= 0.24 \times 40 \text{ g} = 9.60 \text{ g } MgO$$

Practical yield of $MgO = 8 \text{ g } MgO$

$$\therefore \% \text{ purity} = \frac{8}{9.6} \times 100 = 83\%$$

40. (b): 1 mole water = 6.02×10^{23} molecules

\therefore 18 moles water = $18 \times 6.02 \times 10^{23}$ molecules

so, 18 moles water has maximum number of molecules.

41. (c): ψ represents an orbital. ψ_{640} means $n = 6$, $l = 4$, $m = 0$, i.e., 6g orbital.

42. (d)

43. (a): Both statements are correct because atomic

$$\text{mass of metal} = \frac{6.4}{\text{specific heat of metal}}$$

44. (a)

45. (d)





YOUR WAY **CBSE XI**



Series 4

CHAPTERWISE UNIT TEST : ORGANIC CHEMISTRY—SOME BASIC PRINCIPLES AND TECHNIQUES |
HYDROCARBONS | ENVIRONMENTAL CHEMISTRY

GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- (iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 17 are also short answer questions and carry 3 marks each.
- (v) Q. no. 18 is a value based question and carries 4 marks.
- (vi) Q. no. 19 and 20 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.

1. Write the names of the products obtained when C—Cl bond of ethyl chloride undergoes heterolytic fission.
 2. Why do the C—C bonds rather than the C—H bonds break during pyrolysis of alkanes?
 3. What are primary and secondary pollutants?
 4. For testing halogens in an organic compound with AgNO_3 solution (Lassaigne's test), sodium extract is acidified with dilute HNO_3 . What will happen if the extract is acidified with dilute H_2SO_4 in place of dilute HNO_3 ?
 5. Acetylene is acidic but it does not react with NaOH or KOH . Give reason.
 6. An alkane has the molecular mass equal to 72 g/mol. Give the possible structural isomers along with their IUPAC names.
- OR**
- A reaction is carried out using aniline as a reactant as well as a solvent. How will you remove unreacted aniline?
7. Compound (A), C_6H_{12} decolourises bromine dissolved in carbon tetrachloride. Reaction of (A) with alkaline KMnO_4 yields only (B) which is potassium salt of an acid. Write the structures and IUPAC names of the compounds (A) and (B).
 8. What do you understand by Greenhouse effect? What are the major Greenhouse gases?
 9. Which of the two, $\text{O}_2\text{NCH}_2\text{CH}_2\text{O}^-$ or $\text{CH}_3\text{CH}_2\text{O}^-$ is expected to be more stable and why?
 10. Explain why the following systems are not aromatic?
 - (i)
 - (ii)
 11. (i) What is smog? How is classical smog different from photochemical smog?
(ii) What are biodegradable and non-biodegradable pollutants?
 12. (i) Explain how the following mixtures can be separated :
 - (a) Benzoic acid and naphthalene
 - (b) *o*-Nitrophenol and *p*-nitrophenol

- (ii) The R_f values of A and B in a mixture determined by TLC in a solvent mixture are 0.65 and 0.42 respectively. If the mixture is separated by column chromatography using the same solvent mixture as a mobile phase, which of the two components, A or B, will elute first? Explain.

13. How will you prepare *cis*-pent-2-ene and *trans*-pent-2-ene by starting with ethyne?

14. (i) What do you mean by ozone hole? What are its consequences?

(ii) From where does ozone come in the photochemical smog?

15. Give reasons for the following :

(i) SO_3 acts as an electrophile.

(ii) Lassaigne's test is not successful for diazonium salts.

(iii) Alkyl groups act as electron donors when attached to a π -system.

16. (i) Explain the following :

(a) *tert*-Butylbenzene does not give benzoic acid on oxidation with acidic KMnO_4 .

(b) $\text{CH}_2=\text{CH}^-$ is more basic than $\text{HC}\equiv\text{C}^-$.

(ii) Predict the major product in the following reaction :



OR

(i) How will you convert benzene into

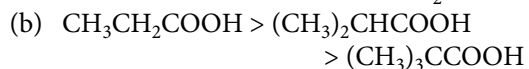
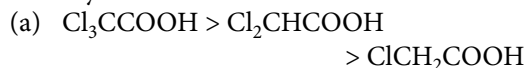
(a) *p*-nitrobromobenzene

(b) *m*-nitrochlorobenzene?

(ii) Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitution reactions with difficulty?

17. (i) Explain the terms inductive effect and electromeric effect.

(ii) Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?



18. Ms. Disha Agnihotri, a senior science teacher delivered a lecture on 'benign by design' topic to class 12 students during the science week. She explained in detail how green chemistry reduces pollution through fundamental breakthroughs

in designing and redesigning chemical processes with an eye towards making them environment friendly.

(i) What values are displayed by the teacher?

(ii) What is Green chemistry?

(iii) Explain how green chemistry can be applied to

(a) reduce the use of synthetic detergents

(b) reduce the use of halogenated solvents in dry cleaning and that of chlorine in bleaching?

19. (i) Explain the following :

(a) Sodium extract is made acidic with acetic acid before the addition of lead acetate in the test of sulphur.

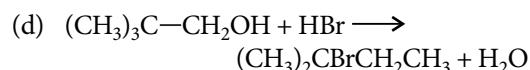
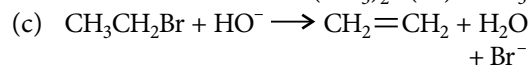
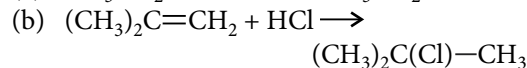
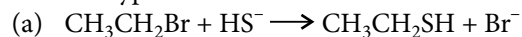
(b) In the test of nitrogen, freshly prepared solution of ferrous sulphate is always used.

(c) During the test for halogens, sodium extract is first boiled with a few drops of conc. HNO_3 .

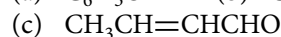
(ii) In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

OR

(i) Classify the following reactions in one of the reaction types.

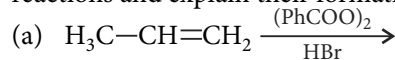


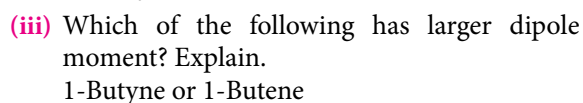
(ii) Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.



20. (i) An alkene 'A' contains three C—C σ -bonds, eight C—H σ -bonds, and one C—C π -bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write the IUPAC name of 'A'.

(ii) Predict the major products of the following reactions and explain their formation.

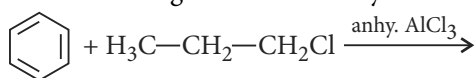




(i) Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+ .

- (b) Toluene, *p*-nitrotoluene, *p*-dinitrobenzene

- (ii) What will be the product obtained as a result of the following reaction and why?



- (iii) How will you convert hexane into benzene?

- $$\text{CH}_3\text{CH}_2\text{-Cl} \xrightarrow{\text{Heterolytic cleavage}} \text{CH}_3\text{CH}_2^+ + \text{Cl}^-$$

Ethyl chloride Ethyl carbocation Chloride ion

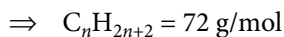
2. Bond energy of C—C bonds (83.0 kcal/mol) is lower than the bond energy of C—H bond (98.8 kcal/mol) thus, C—C bonds break more easily than C—H bonds.

3. Primary pollutants are those which enter directly into the atmosphere due to natural or human activity, *e.g.*, NO while secondary pollutants are those which are formed as a result of reaction between primary pollutants, *e.g.*, PAN (Peroxyacetyl nitrates).

4. Silver sulphate (Ag_2SO_4) will be precipitated in place of silver halide and white precipitate will be formed even in the absence of halogen.

5. Acetylene is a very weak acid thus, it does not react with NaOH or KOH but reacts with a very strong base such as NaNH_2 .

6. Molecular mass of alkane = 72 g/mol.



or $12n + 2n + 2 = 72$ or $n = 5$,

So, the alkane is C_5H_{12} .

Structural isomers are :

- (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (Pentane)

- (ii) $\text{CH}_3-\underset{\cdot}{\text{CH}}-\text{CH}_2\text{CH}_3$ (2-Methylbutane)



- (iii) $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$ (2,2-Dimethylpropane)



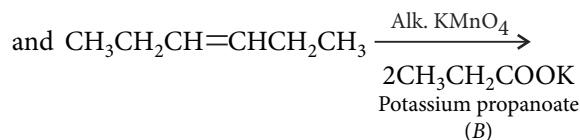
The boiling point of aniline is very high (457 K). If aniline (large excess) is distilled from a small amount of the product by simple distillation, it may cause decomposition of the product. Therefore, to avoid decomposition of the product, aniline is removed either by vacuum distillation or by steam distillation.

7. The molecular formula C_6H_{12} suggests that the compound (A) may be an alkene or a cycloalkane.

As (A) decolourises Br_2 dissolved in CCl_4 , it must be an alkene.

Oxidation of (A) with alkaline KMnO_4 yields only one salt of an acid, the alkene (A) must be symmetrical, *i.e.*, hex-3-ene.

Reactions are as follows :

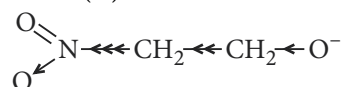


8. The warming of the earth or global warming due to re-emission of sun's energy absorbed by the earth followed by its absorption by CO_2 molecules and H_2O vapour present near the earth's surface and then its radiation back to the earth is called greenhouse effect.

Though CO_2 is the main gas responsible for greenhouse effect, there are some other greenhouse gases also, *e.g.*, methane, chlorofluorocarbons, ozone, nitrous oxide and water vapours.

9. $\text{O}_2\text{N}-\underset{\text{I}}{\text{CH}_2}-\text{CH}_2-\text{O}^-$ $\text{CH}_3-\underset{\text{II}}{\text{CH}_2}-\text{O}^-$

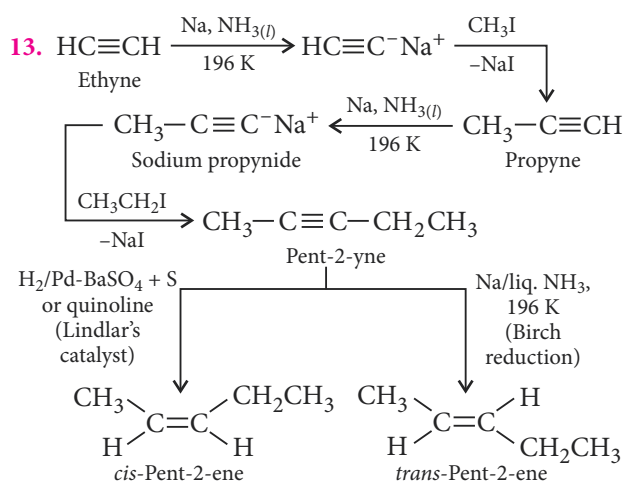
Any ion, whether positively charged or negatively charged, is stable if it is somehow able to diminish the charge appearing on it or, is able to delocalise (spread) the charge on more than one atom. This dispersal/delocalisation of negative charge happens in (I) due to the presence of —NO_2 group which is electron withdrawing in nature. Due to this electron withdrawal, the charge on the oxygen atom is dispersed and the ion (I) becomes more stable as compared to ion (II).



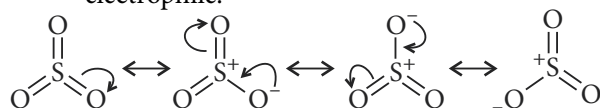
10. (i) Due to the presence of sp^3 hybridised carbon, the system is not planar hence, it is not aromatic.



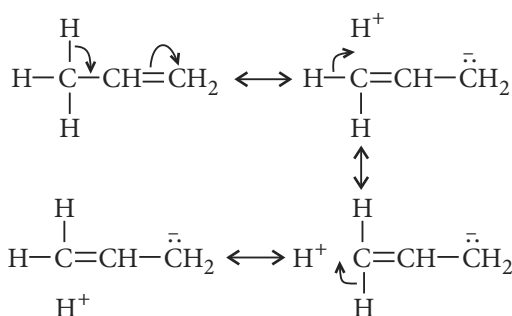
- (ii) Cyclooctatetraene is tub-shaped *i.e.*, not planar and has 8π electrons. Therefore, the system is not aromatic.
11. (i) The presence of smoke in fog is called smog. Classical smog occurs in cool and humid climate when smoke and SO_2 are suspended in air and it is reducing in nature. On the other hand, photochemical smog occurs in warm, dry and sunny climate. It is produced by the action of light on unsaturated hydrocarbons and NO_x in air and, it is oxidising in nature.
- (ii) Biodegradable pollutants are decomposed by bacteria while non-biodegradable pollutants cannot be decomposed or they degrade slowly.
12. (i) (a) Both these solids undergo sublimation on heating. So, the mixture is heated with water, when only benzoic acid dissolves. Upon filtration naphthalene is separated. The solution on cooling gives the crystals of benzoic acid. Alternatively, the mixture is treated with strong aqueous NaOH (or NaHCO_3) solution. The benzoic acid is converted into sodium benzoate while naphthalene is unaffected. The naphthalene is separated by filtration. The filtrate is treated with dil. HCl to regenerate benzoic acid.
- $$\text{C}_6\text{H}_5\text{COOH} + \text{NaOH}_{(aq.)} \longrightarrow \text{C}_6\text{H}_5\text{COONa} + \text{H}_2\text{O}$$
- $$\text{C}_6\text{H}_5\text{COONa} + \text{HCl}_{(dil.)} \longrightarrow \text{C}_6\text{H}_5\text{COOH} + \text{NaCl}_{(aq.)}$$
- (b) *o*-Nitrophenol and *p*-nitrophenol can be separated by steam distillation. *o*-nitrophenol being volatile distills over along with water while *p*-nitrophenol being non-volatile remains in the flask.
- (ii) Since the R_f value of 'A' is 0.65, therefore it is less strongly adsorbed as compared to component 'B' with R_f value of 0.42. Therefore, on extraction of the column, 'A' will elute first.



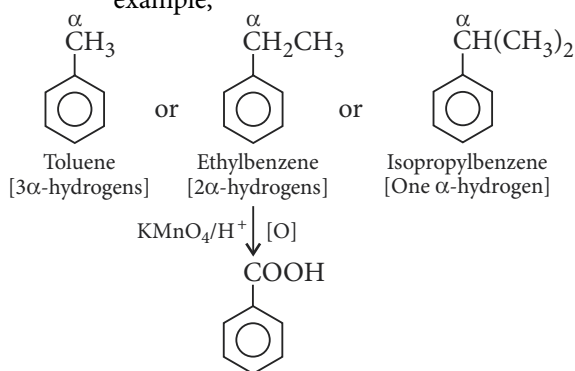
14. (i) The depletion of ozone layer is termed as ozone hole. It was first reported by a group of scientists working in Antarctica in 1980s. Ozone layer is responsible for prevention of infiltration of UV rays which has the potential to cause serious damage to plants, animals and human life. Due to depletion of this O_3 layer, these harmful rays will find an easy route into the earth's atmosphere and create problems such as mutation of cells leading to cancer of the skin or increased transpiration in plants and reduced water level in soil. Increase in UV radiations damages paints and fibres causing them to fade faster.
- (ii) In presence of sunlight, NO_2 present in the air undergoes photolysis to form NO and atomic oxygen. The atomic oxygen then combines with the molecular oxygen to form ozone.
- $$\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}, \quad \text{O} + \text{O}_2 \longrightarrow \text{O}_3$$
15. (i) Due to resonance, sulphur acquires positive charge and therefore, SO_3 acts as an electrophile.



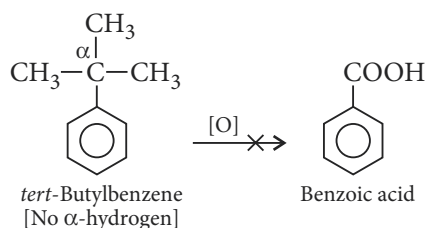
- (ii) Diazonium salts, $\text{C}_6\text{H}_5\text{N}_2^+\text{X}^-$, are unstable and reactive compounds. Therefore, when heated in a fusion tube with sodium to prepare Lassaigne's extract, they immediately get decomposed to give N_2 gas and therefore, NaCN is not formed.
- (iii) Due to hyperconjugation, alkyl groups act as electron donors when attached to a π -system as shown :



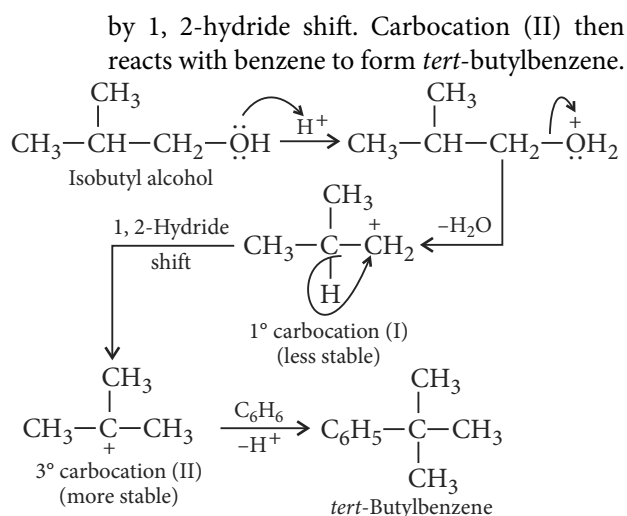
16. (i) (a) Alkylbenzenes in which the alkyl groups contain one or more α -hydrogens or benzylic hydrogen on vigorous oxidation with acidic KMnO_4 ultimately give the corresponding benzoic acids irrespective of the length of the carbon chain. For example,



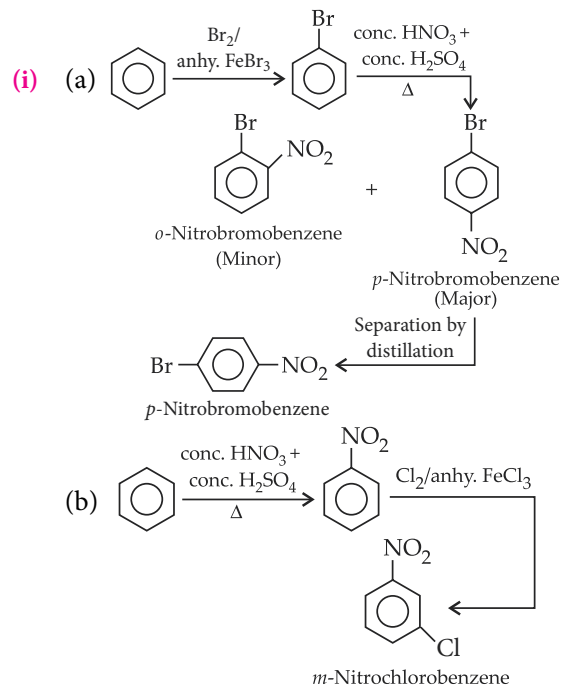
tert-Butylbenzene, on the other hand, does not contain any α -hydrogen or benzylic hydrogen and hence does not undergo oxidation easily to give benzoic acid.



- (b) $\text{CH}_2=\text{CH}^-$ is the conjugate base of the acid $\text{H}_2\text{C}=\text{CH}_2$ and $\text{HC}\equiv\text{C}^-$ is the conjugate base of the acid $\text{HC}\equiv\text{CH}$. We know that stronger the acid, weaker is the conjugate base. Since, $\text{HC}\equiv\text{CH}$ is stronger acid than $\text{CH}_2=\text{CH}_2$, therefore, $\text{CH}_2=\text{CH}^-$ is a stronger base than $\text{HC}\equiv\text{C}^-$.
- (ii) In presence of conc. H_2SO_4 , isobutyl alcohol first gives 1° carbocation (I) which then rearranges to the more stable 3° carbocation (II)



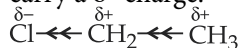
OR



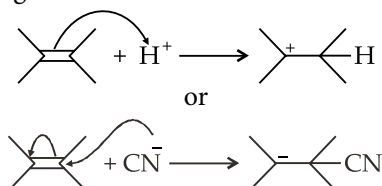
- (ii) Due to the presence of electron cloud containing 6π -electrons above and below the plane of the ring, benzene is a rich source of electrons. Consequently, it attracts the electrophiles towards it and repels nucleophiles. As a result, benzene undergoes electrophilic substitution reactions easily and nucleophilic substitution reactions with difficulty.

17. (i) Inductive effect : Polarisation of σ -bond due to the electron donating or electron withdrawing nature of groups attached is called inductive effect.
e.g., Attachment of Cl, an electronegative atom

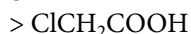
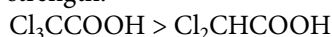
to an ethane molecule causes the carbons to carry a δ^+ charge.



Electromeric effect : In the presence of an attacking reagent, the π -electron cloud in a multiple bonded compound tends to get polarised. Such an effect is termed as temporary effect and the original condition is restored if the reagent is removed.



- (ii) (a) The given order of acidity can be explained by $-I$ effect. Cl is an electronegative atom which withdraws electrons from the adjacent carbon atom. This in turn pulls electrons from the carboxylic group which results in increased acidity. Thus, more the number of Cl atoms, higher is the acidic strength.



- (b) This is an example of $+I$ effect. $-\text{CH}_3$ group is an electron donating group and increases the electron density of the adjacent carbon and this transfers the electron density on the $-\text{COOH}$ group. As a result, the release of H as H^+ becomes difficult and the acidity decreases.

So, if the number of such $-\text{CH}_3$ groups is more on the α -carbon, then the acidic strength decreases.

18. (i) The teacher showed her concern towards the environment and tried to spread awareness regarding green chemistry.
- (ii) Green chemistry can be defined as the design, development and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and environment.
- (iii) (a) Soaps should be used in place of detergents because soaps are 100% biodegradable and do not cause any pollution problem. Nowadays, soft detergents are available which are biodegradable. They can be used in place of 'hard detergents' which are non-biodegradable.
- (b) In dry cleaning, liquefied CO_2 along with

a suitable detergent should be used and for bleaching, hydrogen peroxide should be used which gives better results and is not harmful.

19. (i) (a) Lead acetate is hydrolysed by NaOH present in sodium extract. It is neutralised first with acetic acid before the addition of lead acetate.
- (b) Ferrous sulphate gets hydrolysed if its solution is stored.
- (c) During the test for halogens, sodium extract is first boiled with a few drops of conc. HNO_3 to decompose NaCN or Na_2S if present in the sodium extract.

- (ii) Mass of organic sulphur compound = 0.468 g

$$\text{Mass of BaSO}_4 = 0.668 \text{ g}$$

$$1 \text{ mol of BaSO}_4 = 233 \text{ g}$$

$$233 \text{ g of BaSO}_4 \text{ contains } 32 \text{ g of S.}$$

$$\therefore 0.668 \text{ g of BaSO}_4 \text{ contains}$$

$$\frac{0.668 \times 32}{233} = 0.09174 \text{ g}$$

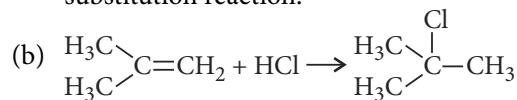
0.09174 g S is present in 0.468 g of the compound.

$$\Rightarrow \% \text{ of S in compound} = \frac{0.09174}{0.468} \times 100 = 19.6\%$$

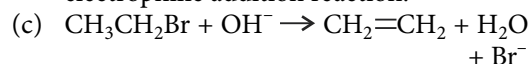
OR

- (i) (a) $\text{CH}_3\text{CH}_2\text{Br} + \text{SH}^- \longrightarrow \text{CH}_3\text{CH}_2\text{SH} + \text{Br}^-$

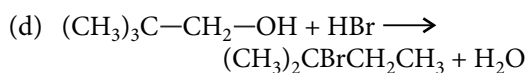
Here HS^- , a nucleophile displaces Br^- from the bromoalkane. Since, the reaction is brought about by a nucleophile and substitution occurs thereafter, the reaction will be termed as a nucleophilic substitution reaction.



Here, alkene due to its high electron density undergoes electrophilic attack. Thus, H^+ and Cl^- ions are added to the alkene. Hence, the reaction is an electrophilic addition reaction.

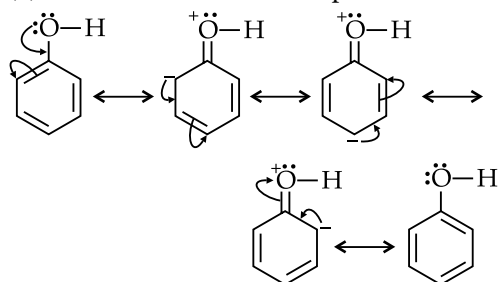


Here, there is no atom which is displaced or substituted. Although the reaction is brought about by a nucleophile OH^- , it is not a nucleophilic substitution. It is an elimination reaction as HBr molecule has been removed from the reactant.

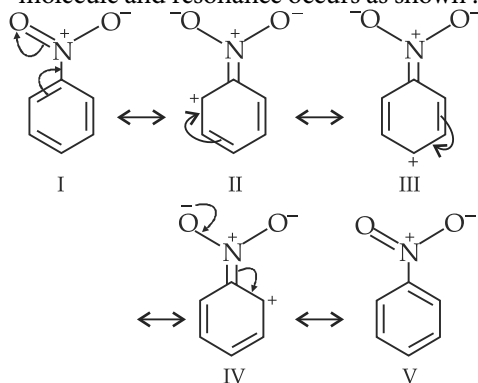


This is an example of a rearrangement followed by nucleophilic substitution. Initially, a 1° carbocation is formed which rearranges to produce a more stable 3° carbocation. Finally, Br^- attacks the carbocation and product is formed.

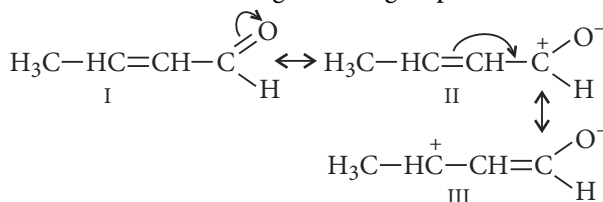
(ii) (a) Resonance structures of phenol are :



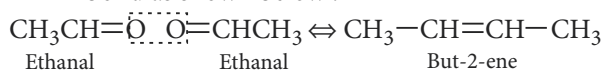
(b) $-\text{NO}_2$ is an electron withdrawing group. As a result, it polarises the benzene molecule and resonance occurs as shown :



(c) $\text{CH}_3\text{CH}=\text{CHCHO}$ is an α, β -unsaturated aldehyde where the $\text{C}=\text{C}$ gets polarised due to the neighbouring electron withdrawing $-\text{CHO}$ group.

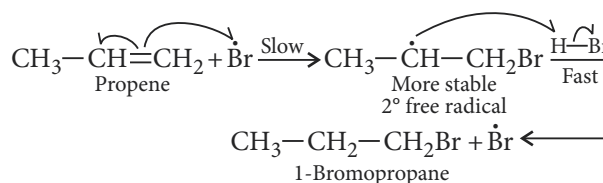


20. (i) An aldehyde with molar mass of 44 u is ethanal, $\text{CH}_3\text{CH}=\text{O}$. Thus, the alkene 'A' which on ozonolysis gives two moles of ethanal can be formed by removing oxygen atoms from two moles of ethanal and joining them by a double bond as shown below :

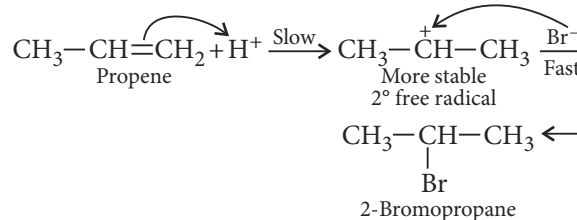


As required, but-2-ene has three $\text{C}-\text{C}$ σ -bonds, eight $\text{C}-\text{H}$ σ -bonds and one $\text{C}-\text{C}$ π -bond.

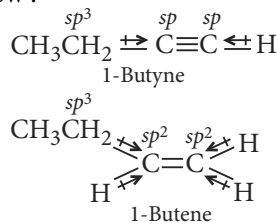
(ii) (a) In presence of peroxide, addition of HBr to propene follows anti-Markovnikov's rule and hence, gives 1-bromopropane as the major product. The reaction occurs through a free radical mechanism *via* a more stable free radical intermediate as shown in the reaction :



(b) In absence of peroxides, addition of HBr to propene follows Markovnikov's rule and hence, gives 2-bromopropane as the major product. The reaction occurs through ionic mechanism *via* a more stable carbocation intermediate as shown below :



(iii) The direction of dipole moments of individual bonds in 1-butyne and 1-butene are shown below :



The resultant dipole moment of both 1-butyne and 1-butene is due to the dipole moments of $\text{CH}_3\text{CH}_2-\text{C}$ and $\text{C}-\text{H}$ bonds which oppose each other. Since a sp carbon is more electronegative than a sp^2 carbon, therefore, the dipole moment of $\text{CH}_3\text{CH}_2-\text{C}$ bond in 1-butyne is more than that of $\text{CH}_3\text{CH}_2-\text{C}$ bond in 1-butene. As a result, the dipole moment of 1-butyne is more than that of 1-butene.

OR

Contd. on page no.77

EXAMINER'S MIND

CLASS XI



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

p-BLOCK ELEMENTS | ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- CO₂ is isostructural with
(a) HgCl₂ (b) SnCl₂
(c) C₂H₄ (d) NO₂
- The IUPAC name of $\text{H}_2\text{N}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_2-\text{COOH}$ is
(a) 3-amino-3-oxopropanoic acid
(b) 3-amidopropanoic acid
(c) 2-amidoethanoic acid
(d) 2-carbamoylethanoic acid.
- Which of the following substances does not act as a Lewis acid?
(a) AlCl₃ (b) SnCl₄
(c) FeCl₃ (d) AlCl₃·6H₂O
- In which of the following two carbon atoms are differently hybridised?
 $\text{CH}_2=\overset{+}{\text{C}}\text{H}$ (I) $\text{CH}_3-\overset{-}{\text{C}}\text{HCH}_3$ (II) $\text{CH}_2=\overset{-}{\text{C}}\text{H}$ (III)
 $\text{CH}\equiv\overset{-}{\text{C}}$ (IV) $\overset{\cdot}{\text{C}}(\text{CH}_3)_3$ (V)
 (a) I only (b) II and V
 (c) III only (d) I and V
- When Sn is treated with conc. HNO₃
(a) it is converted into stannous nitrate
(b) it is converted into stannic nitrate
(c) it is converted into metastannic acid
(d) it becomes passive.
- Prussian blue can be represented as $\text{Fe}[\text{Fe}(\text{CN})_6]^-$
 $\begin{array}{c} \uparrow \quad \uparrow \\ x \quad y \end{array}$
 Oxidation numbers of Fe atoms indicated by x and y are respectively
 (a) 2, 2 (b) 2, 3
 (c) 3, 2 (d) 3, 3
- When PbO₂ is reacted with HCl then the gas coming out is
(a) O₂ (b) Cl₂
(c) H₂ (d) CO + H₂
- Which of the following statements is false?
(a) Feeble acids and bases are weaker than H₂O.
(b) Weak acids are weaker than H₃O⁺ but stronger than H₂O.
(c) Weak bases are weaker than OH⁻ but stronger than H₂O.
(d) None of these.
- Select the incorrect statement.
(a) B₂H₆ has all B—H bonds equal.
(b) AlH₃ is colourless solid and is polymeric containing Al—H—Al bridges.
(c) LiAlH₄ is an ionic compound.
(d) Aluminium halides (AlX₃ where X = Cl, Br, I) have low melting points, are covalent and have the halogen-bridged dimeric structures.
- Which of the following statements is correct?
(a) Singlet dimethylcarbene [(CH₃)₂C:] is more stable than the triplet [(CH₃)₂C·].
(b) Singlet difluorocarbene [F₂C:] is less stable than the corresponding triplet.
(c) Singlet carbene resembles free diradical while triplet carbene resembles a carbocation.
(d) None of these.
- Dry powder fire extinguisher contains
(a) sand
(b) sand and Na₂CO₃
(c) sand and baking soda
(d) sand and K₂CO₃.

12. Arrange the following in decreasing order of solubility in water.

(a) I > III > II

(b) III > II > I

(c) II > III > I

(d) All are equally soluble



13. Mixture of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ can be separated by :

(a) HCl

(b) NH_4OH

(c) NaOH

(d) HNO_3

14. Which of the following is not stabilised by hyperconjugation?

(a) $\text{CH}_3-\text{CH}_2^+$

(b)

(c)

(d)

15. Which of the following is true?

(a) Coke is found in nature.

(b) Producer gas is a mixture of CO and H_2 .

(c) CO is used in the extraction of Ni by Mond's process.

(d) CO_2 can be prepared by dehydration of formic acid.

16. Solubility of an organic compound in water is 10 g/100 mL at 20°C and 60 g/100 mL at 70°C . 30 g of an impure organic compound is dissolved in 50 mL of water at 70°C and cooled to 20°C . Crystals formed weigh

(a) 5 g

(b) 20 g

(c) 25 g

(d) 30 g

17. Which of the following statements is incorrect?

(a) The *meta*-position in nitrobenzene undergoes electrophilic substitution reaction because it is less deactivated when compared to *ortho* and *para* positions in nitrobenzene.

(b) The *meta*-position in phenol is more electron rich than the *meta*-position in nitrobenzene.

(c) The benzene ring in is slightly deactivated than the benzene ring in .

(d) CF_3^+ is less stable than CF_3CH_2^+ .

18. The correct order of increasing stability of the following carbanions is

$\text{CH}_2=\text{CH}\text{CH}_2^-$ (I) $\text{CH}_2=\text{CH}^-$ (II) $(\text{CH}_3)_3\text{C}^-$ (III)

Ph_3C^- (IV)

CH_3^- (V)

(a) III < V < II < IV < I

(b) II < III < V < IV < I

(c) II < III < V < I < IV

(d) III < V < II < I < IV

19. Borazine $\text{B}_3\text{N}_3\text{H}_6$ (A) is converted into disubstituted product $\text{B}_3\text{N}_3\text{H}_4\text{X}_2$ (B). Number of isomers of 'B' would be

(a) 2

(b) 4

(c) 6

(d) none of these.

20. Organic compound of the molecular formula $\text{C}_2\text{H}_2\text{Br}_2$ can exist in how many isomeric forms?

(a) 1

(b) 2

(c) 3

(d) 4

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. Which of the following equilibria represent(s) the actual source of proton in boric acid?

(a) $\text{B}(\text{OH})_3(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + [\text{B}(\text{OH})_4]^- (\text{aq})$

(b) $3\text{B}(\text{OH})_3(\text{aq}) \rightleftharpoons [\text{B}_3\text{O}_3(\text{OH})_4]^- (\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
(In neutral or basic solution)

(c) $\text{B}(\text{OH})_3 \rightleftharpoons \text{H}_2\text{BO}_3^+ + \text{H}^+$

(d) All of the above

22. Which of the following statement(s) is/are correct?

(a) HCN and HNC are functional isomers.

(b) HCN and HNC are tautomers.

(c) $\text{R}-\text{CN}$ and $\text{R}-\text{NC}$ are functional isomers.

(d) R_3N^+ shows $-I$ effect.

23. Which of the following is/are sub-oxides?

(a) C_3O_2

(b) N_2O

(c) PbO_2

(d) CO_2

24. Which of the following have zero dipole moment?

(a) *p*-Dichlorobenzene

(b) Benzene-1, 4-diol

(c) Fumaric acid

(d) Maleic acid

25. The difference in properties of CH_4 and SiH_4 is due to

(a) large difference in the electronegativity of carbon and silicon

(b) large difference in size of carbon and silicon atoms

(c) the inability of carbon to expand its octet

(d) the inability of silicon to form double bonds.

SECTION - III

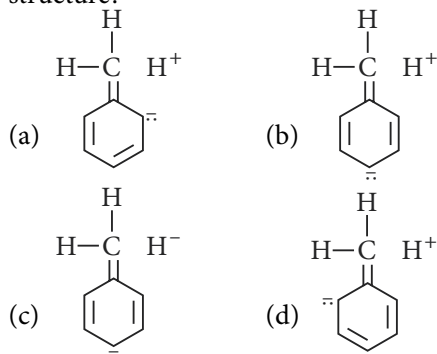
Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Hyperconjugation is a general stabilising interaction. It involves delocalisation of s -electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p -orbital. The s -electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p -orbital. Hyperconjugation is a permanent effect.

26. Which of the following is incorrect hyperconjugative structure?



27. Which of the following has highest heat of hydrogenation?

- (a) Ethylene (b) But-1-ene
(c) Isobutylene (d) Tetramethylethylene

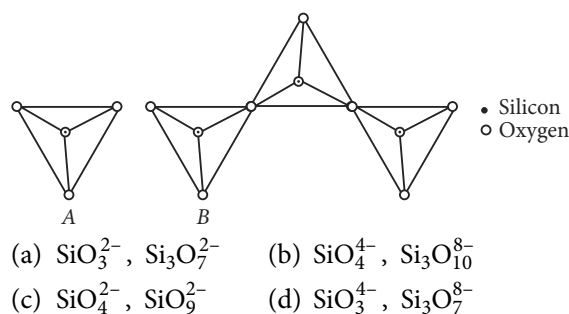
28. Which of the following has highest heat of combustion?

- (a) Isobutylene (b) But-1-ene
(c) Tetramethylethylene (d) But-2-ene

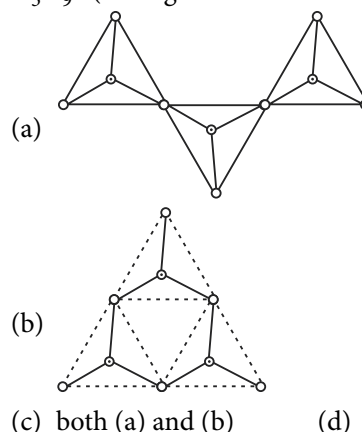
Paragraph for Questions 29 to 31

The basic structural unit of silicates is SiO_4^{4-} in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion. In silicates, either the discrete unit is present or a number of such units are joined together *via* corners by sharing 1, 2, 3 or 4 oxygen atoms per silicate unit. When silicate units are linked together, they form chain, ring, sheet or three-dimensional structures.

29. Structures 'A' and 'B' represent different silicate anions. Their formulae are respectively



30. $\text{Si}_3\text{O}_9^{6-}$ (having three tetrahedra) is represented as



31. The silicate anion in the mineral kinoite is a chain of three SiO_4^{4-} tetrahedra that share corners with adjacent tetrahedra. The mineral also contains Ca^{2+} ions, Cu^{2+} ions, and water molecules in a 1 : 1 : 1 ratio. The mineral is represented as

- (a) $\text{CaCuSi}_3\text{O}_{10} \cdot \text{H}_2\text{O}$
(b) $\text{CaCuSi}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$
(c) $\text{Ca}_2\text{Cu}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$
(d) none of these.

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the compounds given in List I with their uses given in List II and select the correct answer using the code given below the lists :

List I	List II
P. Boric acid	1. Friedel-Crafts acylation
Q. Borax	2. Mild antiseptic
R. Aluminium chloride	3. Washing powder
S. Sodium peroxoborate	4. Buffer

	P	Q	R	S
(a)	1	2	3	4
(b)	2	3	4	1
(c)	2	4	1	3
(d)	4	3	2	1

33. Match the phenomena given in List I with their descriptions given in List II and select the correct answer using the code given below the lists :

List I	List II
P. Inductive effect	1. Delocalisation of σ electrons with π -bond
Q. Resonance	2. Strong effect
R. No bond resonance	3. Permanent effect
S. Electromeric effect	4. Delocalisation of π -electrons

	P	Q	R	S
(a)	1	4	3	2
(b)	4	3	1	2
(c)	3	4	1	2
(d)	1	4	3	2

34. Match the List I with List II and select the correct answer using the code given below the lists :

List I	List II
P. C_8K	1. Producer gas
Q. SiC	2. Paramagnetic
R. $CO + N_2$	3. Carborundum
S. CO, H_2, CO_2, CH_4	4. Coal gas

	P	Q	R	S
(a)	2	3	1	4
(b)	1	2	3	4
(c)	4	3	2	1
(d)	2	1	4	3

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.

35. **Assertion :** Tl^{3+} acts as an oxidising agent.
Reason : Due to inert pair effect, Tl^+ is more stable than Tl^{3+} .

36. **Assertion :** In case of volatile compounds, vapour density is one-half of the molecular weight.

Reason : Vapour density is the other name of density.

37. **Assertion :** Hybridisation of boron in B_2H_6 is sp^3 and geometry of boron is tetrahedral.

Reason : Three centre-two electron bonds are present in B_2H_6 molecule.

38. **Assertion :** Lithium is not used in Lassaigne's test.

Reason : Lithium generally forms covalent compounds.

39. **Assertion :** Many metals produce coloured beads with borax.

Reason : Borax forms a glassy bead on heating which optically influences light in a way that is characteristic of the metal involved.

40. **Assertion :** Heterolytic fission of $CH_3CH_2CH_3$ gives $CH_3CH_2^+$ and CH_3^- .

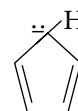
Reason : $CH_3CH_2^+$ is more stable than CH_3^+ , but $CH_3CH_2^-$ is less stable than CH_3^- .

SECTION - VI

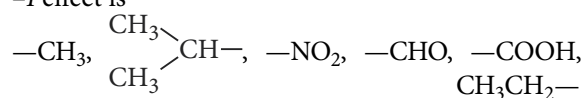
Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. Number of resonating structures possible in isopropyl carbocation is
 42. Number of electrons transferred to vacant $2p$ -orbital of boron by fluorine in BF_3 is
 43. Deep violet coloured complex formed when sodium extract of the organic compound containing sulphur is treated with sodium nitroprusside has the formula $Na_2[Fe(CN)_xNOS]$. The value of x is
 44. When diborane reacts with excess of ammonia at low temperature, then it gives $B_2H_6 \cdot 2NH_3$ which is comprised of x number of ions. The value of x is
 45. Number of π -electrons in the following structure is



46. Percentage of CO_2 in carbogen mixture used in treatment of central retinal artery occlusion is
 47. Number of groups amongst the following that show $-I$ effect is



48. When stannous oxalate is heated then the number of gaseous products formed is
49. In a compound C, H and N are present in 9 : 1 : 3.5 by weight. If molecular weight of the compound is 108, the number of N atoms present in the molecular formula will be
50. In the compound beryl, number of oxygen atoms shared by one silicate tetrahedron is

SOLUTIONS

1. (a) : CO_2 is isostructural with HgCl_2 because both have linear structure.

2. (d) : $\text{H}_2\text{NOC}-\overset{2}{\text{CH}_2}-\overset{1}{\text{COOH}}$
2-Carbamoylethanoic acid

3. (d) : $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ does not act as a Lewis acid because it exists as $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$, i.e., Al^{3+} forms coordinate bonds with $6\text{H}_2\text{O}$ molecules. AlCl_3 is electron deficient because octet of Al is not complete therefore, it acts as a Lewis acid. SnCl_4 is electron deficient because it has vacant d -orbitals and can accept negatively charged ion. Hence, it is a Lewis acid. FeCl_3 is electron deficient because its octet is not complete therefore, it is a Lewis acid.

4. (d) : $\text{CH}_2=\overset{+}{\text{CH}}$ $\text{CH}_3\overset{-}{\text{C}}\text{HCH}_3$ $\text{CH}_2=\overset{-}{\text{CH}}$
 sp^2 sp sp^3 sp^3 sp^2 sp^2
I II III
 $\text{CH}\equiv\overset{-}{\text{C}}$ $\overset{\cdot}{\text{C}}(\text{CH}_3)_3$
 sp sp sp^2 sp^3
IV V

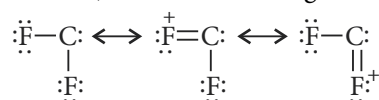
5. (c) : $\text{Sn} + 4\text{HNO}_3 \longrightarrow \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{H}_2\text{O}$
Metastannic acid

6. (c) : Prussian blue, $[\text{Fe}(\text{CN})_6]^-$ is formed when Fe^{3+} salts react with $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$
 $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{4-} \longrightarrow \text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^-$
Thus, $x = 3$ and $y = 2$.

7. (b) : PbO_2 oxidises HCl to Cl_2 .
 $\text{PbO}_2 + 4\text{HCl} \longrightarrow \text{PbCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$
8. (d) : Weak and feeble nature of an acid (or a base) is compared with H_2O which acts both as an acid as well as a base.
In general, weak acid $> \text{H}_2\text{O} >$ feeble acid
weak base $> \text{H}_2\text{O} >$ feeble base

9. (a) : B_2H_6 has two types of bonds :
 α -bond : formed by sharing of two electrons between two B atoms and one H atom.
 β -bond : formed by sharing of two electrons between B and H atoms.
Bond length : α -bond $> \beta$ -bond.

10. (d) : In a triplet carbene, two electrons are present in different orbitals with the result there is less electrostatic repulsion than when both are in the same orbital as in a singlet carbene. Hence, generally a triplet carbene is more stable than the singlet. However, this is reverse in case of difluorocarbenes where a singlet carbene (having empty p -atomic orbital) is more stable than the triplet (not having any empty orbital) because here the lone pair of electrons present in p -atomic orbital of F overlaps laterally with the empty p -atomic orbital of the singlet carbene (stabilisation through resonance).

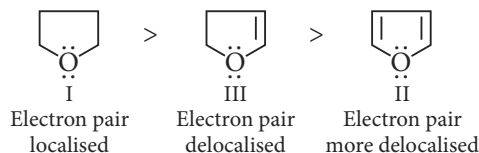


Resonance stabilisation of singlet difluorocarbene

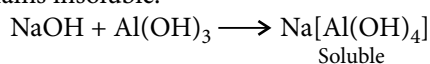
Thus, $(\text{CH}_3)_2\overset{\cdot}{\text{C}} > (\text{CH}_3)_2\text{C:}$ and $\text{F}_2\overset{\cdot}{\text{C}} < \text{F}_2\text{C:}$
Triplet Singlet Triplet Singlet

Also, singlet carbene resembles a carbocation and a triplet carbene resembles a free diradical.

11. (c) : Mixture of sand (SiO_2) and baking soda (NaHCO_3) is used as a dry powder fire extinguisher.
12. (a) : Higher the electron density on O, stronger is the H-bond with water and thus, more is the solubility. Thus, solubility of the three ethers follows the order :



13. (c) : NaOH dissolves $\text{Al}(\text{OH})_3$ while $\text{Fe}(\text{OH})_3$ remains insoluble.



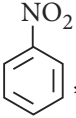
14. (b) : Hyperconjugation is the delocalisation of sigma electrons with π -bond. In carbocation, hyperconjugation is possible only when α -hydrogen is present, so in carbocations (a), (c) and (d) hyperconjugation is possible while (b) is stabilised by the interaction of the cyclopropyl bonding orbitals with the vacant p -orbital of carbon.
15. (c) : Coke is not found in nature. It is an artificial product. CO_2 cannot be formed by dehydration of formic acid.
 $\text{HCOOH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{CO} + \text{H}_2\text{O}$
Producer gas is a mixture of CO and N_2 .
16. (c) : At 70°C , 100 mL water can dissolve organic compound = 60 g

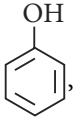
∴ At 70°C, 50 mL water can dissolve organic compound = 30 g


At 20°C, 100 mL water can dissolve organic compound = 10 g


∴ At 20°C, 50 mL water can dissolve organic compound = 5 g



Hence, solute crystallised = (30 - 5) g = 25 g

17. (d): In , the $-\text{NO}_2$ group deactivates the benzene ring, i.e., all the positions are deactivated but the deactivation at *ortho* and *para*-positions are more than that at the *meta*-position.

In , $-\text{OH}$ group activates all the positions in benzene ring but *ortho* and *para* are more activated than *meta*. Hence, *meta*-position in nitrobenzene is deactivated while *meta*-position in phenol is activated. So, *meta*-position in phenol is more electron rich than in nitrobenzene.

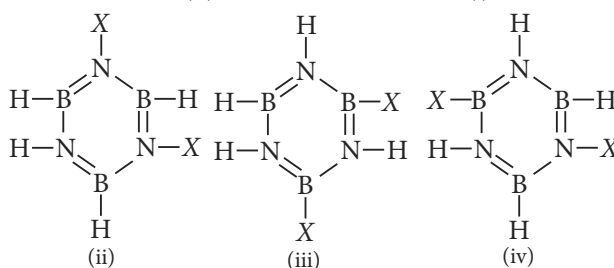
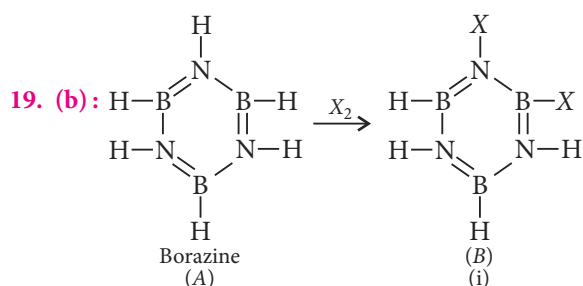
In , due to the lone pair of electrons in conjugation with $-\text{C}-$ group, the

resonating structure is , so

benzene ring is deactivated. Hence, in , the benzene ring is slightly deactivated than the benzene ring in .

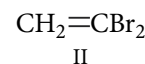
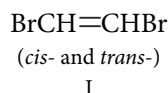
In CF_3^+ , +ve charge is dispersed due to back bonding of lone pair of electrons from fluorine with vacant *p*-orbitals of C while in CF_3CH_2^+ due to $-I$ effect of fluorine, the +ve charge is intensified and thereby, it is destabilised.

18. (d): $(\text{CH}_3)_3\bar{\text{C}} < \bar{\text{C}}\text{H}_3 < \text{CH}_2=\bar{\text{C}}\text{H} < \text{CH}_2=\text{CH}-\bar{\text{C}}\text{H}_2 < \text{Ph}_3\bar{\text{C}}$
- III
V
II
- Least stable due to +I effect
Stable due to -ve charge on electronegative carbon
- I
IV
- Stable due to delocalisation of -ve charge
Most stable due to extensive delocalisation of -ve charge on benzene ring



Four different isomers of 'B' are possible.

20. (c): $\text{C}_2\text{H}_2\text{Br}_2$ can have the following structures :



Structures I and II are position isomers, further structure I (not II) can show geometrical isomerism.

21. (a)

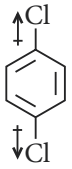
22. (a, b, c, d): Cyanide and isocyanide are different functional groups hence, HCN, HNC and RCN, RNC are functional isomers.

HCN is converted into HNC by 1, 2-hydrogen shift hence, they are tautomers.

In R_3N^+ , nitrogen has +ve charge hence, shows $-I$ effect.

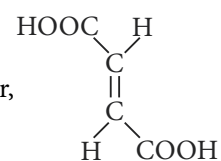
23. (a, b)

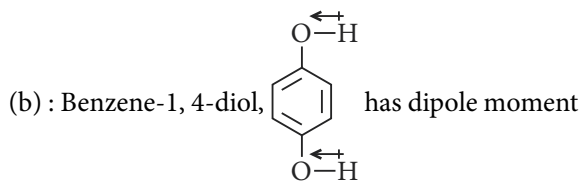
24. (a, c)

(a):  has zero dipole moment as both the dipoles are equal and opposite.

(c): Fumaric acid is *trans*-isomer,

therefore, dipoles get cancelled.





because both —OH groups are not in the same plane, their dipole moments do not get cancelled.

(d) : Maleic acid is *cis*-isomer hence, it cannot have zero dipole moment.

25. (a, c)

26. (c) : When *s*-electrons of C—H bond take part in hyperconjugation, H^- cannot be formed rather H^+ is formed.

27. (a) : Ethylene has highest heat of hydrogenation due to least hyperconjugation as there is no α -hydrogen atom. But-1-ene has two α -hydrogen atoms, isobutylene has six α -hydrogen atoms while tetramethylethylene has 12 α -hydrogen atoms.

28. (b) : Lesser the number of hyperconjugative structures, lesser will be the stability and thus, more will be the heat of combustion.

29. (b) 30. (b)

31. (c) : The formula of silicate anion is $Si_3O_{10}^{8-}$. Thus, the mineral is represented as $Ca_2Cu_2Si_3O_{10} \cdot 2H_2O$.

32. (c)

33. (c) : $P \rightarrow 3$; Inductive effect is a permanent effect.
 $Q \rightarrow 4$; Resonance is the delocalisation of π -electrons.

$R \rightarrow 1$; No bond resonance or hyperconjugation is delocalisation of sigma electrons with π -bond.

$S \rightarrow 2$; Electromeric effect is very strong effect.

34. (a) : $P \rightarrow 2$; C_8K is paramagnetic because C_8^- contains one unpaired electron.

$Q \rightarrow 3$; SiC is carborundum.

$R \rightarrow 1$; A mixture of $CO + N_2$ is producer gas.

$S \rightarrow 4$; A mixture of $CO + H_2 + CO_2 + CH_4$ is coal gas.

35. (a)

36. (c) : Vapour density and density of a volatile organic compound are quite different.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

37. (a) : Due to $2e - 3c$ bond the hybridisation of B is sp^3 and the geometry is tetrahedral.

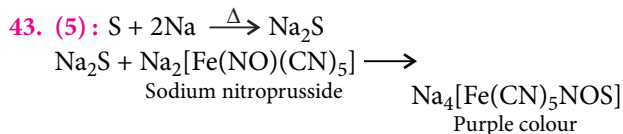
38. (a)

39. (c) : The metal cation on heating with borax bead produces corresponding coloured metaborate.

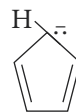
40. (a)

41. (7) : No. of resonating structures
 = No. of hyperconjugative structures + 1.

42. (2) : Fluorine transfers two electrons to vacant $2p$ -orbital of boron thus forming $p\pi-p\pi$ bond.



44. (2) : The compound $B_2H_6 \cdot 2NH_3$ is ionic and comprises of $(H_3N \rightarrow BH_2 \leftarrow NH_3)^+$ and $[BH_4]^-$ ions.

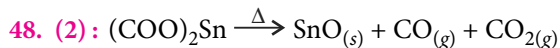


45. (6) :

Cyclopentadienyl anion
 (planar, 6 π -electrons, aromatic)

46. (5) : Carbogen is a mixture of 95% O_2 and 5% CO_2 .

47. (3) : $-NO_2$, $-CHO$ and $-COOH$ groups show $-I$ effect.



Thus, CO and CO_2 are the two gaseous products formed.

49. (2) :

	C	H	N
Weight ratio :	9	: 1	: 3.5
Molar ratio :	$\frac{9}{12}$: $\frac{1}{14}$: $\frac{3.5}{14}$
	$= \frac{3}{4}$: $\frac{1}{1}$: $\frac{1}{4}$

Simplest ratio : 3 : 4 : 1

Empirical formula = C_3H_4N

$(C_3H_4N)_n = 108$

$(12 \times 3 + 1 \times 4 + 14)n = 108$

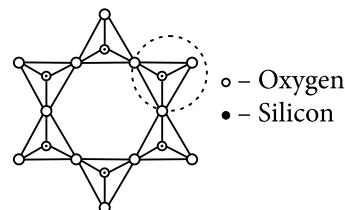
$54n = 108 \Rightarrow n = 108/54 = 2$

Molecular formula = $C_6H_8N_2$

50. (2) : Beryl is a cyclic silicate.

The formula of Beryl is $Be_3Al_2(SiO_3)_6$.

Every SiO_4^{4-} unit shares two O atoms. The structure is

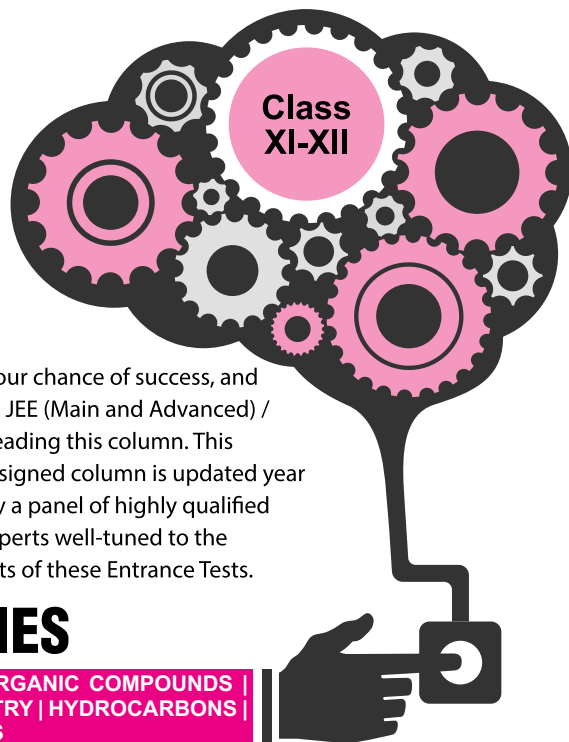


SiO_4^{4-} is sharing two O atoms.



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Unit 6 PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS | SOME BASIC PRINCIPLES OF ORGANIC CHEMISTRY | HYDROCARBONS | ORGANIC COMPOUNDS CONTAINING HALOGENS

PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS

- Methods of Purification of Organic Compounds
- Qualitative Analysis
- Quantitative Analysis
- Calculation of Empirical and Molecular Formula

TIPS TO REMEMBER

Purification

- The organic compounds extracted from natural sources or synthesised in the laboratory are
- The methods commonly used for purification are :

contaminated with small amounts of other similar compounds. In order to characterise them, it is essential to purify them.

- The methods employed for purification depend upon the nature of the substance (whether solid or liquid) and the type of impurities present in it.
- The purity of an organic compound is checked by determining one or more of its physical constants like melting point, boiling point etc.

Method	Used for separating	Examples
Crystallisation	Mixtures with difference in the solubility of the organic compound and its impurities in a solvent.	<ul style="list-style-type: none"> • Sugar with impurity of common salt can be crystallised from hot ethanol (sugar dissolves but salt does not). • Benzoic acid and naphthalene from hot water (benzoic acid dissolves but naphthalene does not).
Sublimation	Mixtures of sublimable volatile compounds and non-sublimable impurities.	<ul style="list-style-type: none"> • Purification of camphor, anthracene, naphthalene, benzoic acid, etc.
Distillation	Mixtures of liquids which boil without decomposition and contains non-volatile impurities.	<ul style="list-style-type: none"> • Chloroform (b.pt. 334 K) and aniline (b.pt. 457 K). • Ether (b.pt. 308 K) and toluene (b.pt. 383 K).
Fractional distillation	Mixtures of two or more miscible liquids which have b.pt. close to each other.	<ul style="list-style-type: none"> • Acetone (b.pt. 330 K) and methyl alcohol (b.pt. 338 K). • Benzene (b.pt. 353 K) and toluene (b.pt. 383 K).

Steam distillation	Mixtures of substances which are (i) volatile in steam, (ii) not miscible with water, (iii) possess a vapour pressure of about 10-15 mm of Hg, (iv) contain non-volatile impurities.	<ul style="list-style-type: none"> Purification of aniline (b.pt. 457 K). Nitrobenzene, <i>o</i>-nitrophenol, bromobenzene, etc.
Azeotropic distillation	Mixtures with constant boiling points-Azeotropic mixtures.	<ul style="list-style-type: none"> Ethanol and water in ratio 95.87 : 4.13.
Vacuum distillation	Mixtures of high boiling liquids which decompose at or below their boiling points.	<ul style="list-style-type: none"> Glycerol from spent-lye in soap industry (at 453 K under 12 mm Hg). Concentration of sugarcane juice.
Chromatography	Mixtures with difference in the rates at which the components of the mixture move through a porous medium.	<ul style="list-style-type: none"> <i>ortho</i> and <i>para</i> nitroanilines. Blue and red dyes. Plant pigments and other natural products.
Differential extraction	Mixtures of organic compounds from their aqueous solutions using a solvent that should (i) be immiscible with water, (ii) dissolve the organic compound.	<ul style="list-style-type: none"> Benzoic acid from its water solution using benzene.

Qualitative Analysis

❑ An organic compound mainly consists of two elements carbon and hydrogen. In addition to these, it may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

❑ The qualitative analysis of organic compounds involves the detection of all these major elements present in it with the help of suitable chemical tests.

Element	Detection	Confirmatory test	Reactions
Carbon	Copper oxide test $2\text{CuO} + \text{C} \xrightarrow{\Delta} 2\text{Cu} + \text{CO}_2\uparrow$	CO_2 gas turns lime water milky.	$\text{CO}_2\uparrow + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3\downarrow + \text{H}_2\text{O}$ Lime water Milkiness
Hydrogen	$\text{CuO} + 2\text{H} \xrightarrow{\Delta} \text{Cu} + \text{H}_2\text{O}$	Water droplets appear on the cooler part of the ignition tube and also turns anhydrous CuSO_4 blue.	$\text{CuSO}_4 + 5\text{H}_2\text{O} \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ White Blue
Nitrogen	Lassaigne's extract (L.E.) $\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN (L.E.)}$	L.E. + FeSO_4 + NaOH , boil and cool + FeCl_3 + conc. HCl . Gives blue or green colour.	$\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4$ $\text{Fe(OH)}_2 + 6\text{NaCN} \longrightarrow \text{Na}_4[\text{Fe(CN)}_6] + 2\text{NaOH}$ $\text{Na}_4[\text{Fe(CN)}_6] + \text{FeCl}_3 \xrightarrow{\text{HCl}} \text{NaFe[Fe(CN)}_6] + 3\text{NaCl}$ Prussian blue or $3\text{Na}_4[\text{Fe(CN)}_6] + 4\text{FeCl}_3 \longrightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{NaCl}$ Prussian blue

Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$ (L.E.)	(i) L.E. + sodium nitroprusside. A deep violet colour. (ii) L.E. + CH_3COOH + $(\text{CH}_3\text{COO})_2\text{Pb}$ Gives a black ppt.	(i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \longrightarrow$ Sodium nitroprusside $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ Deep violet (ii) $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}}$ $\text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$ Black ppt.
Halogens	$\text{Na} + \text{X} \xrightarrow{\Delta} \text{NaX}$ (L.E.)	L.E. + $\text{HNO}_3 + \text{AgNO}_3$ (i) White ppt. soluble in aqueous NH_3 (or NH_4OH) confirms Cl. (ii) Yellow ppt. partially soluble in aqueous NH_3 (or NH_4OH) confirms Br. (iii) Yellow ppt. insoluble in aqueous NH_3 (or NH_4OH) confirms I.	$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$ ppt. $\text{AgCl} \downarrow + 2\text{NH}_3(\text{aq.}) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$ White ppt. Soluble
Nitrogen and sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaSCN}$ (L.E.) Sodium thiocyanate	L.E. + FeCl_3 Blood red colouration confirms presence of N and S both.	$\text{NaSCN} + \text{FeCl}_3 \longrightarrow [\text{Fe}(\text{SCN})]\text{Cl}_2 + \text{NaCl}$ Blood red colour
Phosphorus	$\text{P} \xrightarrow[\Delta]{\text{Na}_2\text{O}_2, \text{boil}} \text{Na}_3\text{PO}_4$	Solution is boiled with nitric acid and then treated with ammonium molybdate $(\text{NH}_4)_2\text{MoO}_4$. Formation of yellow ppt. indicates presence of phosphate (hence, phosphorus) in organic compound.	$\text{Na}_3\text{PO}_4 + 3\text{HNO}_3 \longrightarrow \text{H}_3\text{PO}_4 + 3\text{NaNO}_3$ $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 \longrightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \downarrow +$ Ammonium phosphomolybdate (Yellow ppt.) $21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$

KEY POINT

- Presence of oxygen in an organic compound can be detected indirectly by testing the compound containing functional group such as $-\text{OH}$, $-\text{CHO}$, $>\text{C}=\text{O}$, $-\text{COOH}$, $-\text{NO}_2$, etc.

Quantitative Analysis

- The percentage composition of elements present in an organic compound is determined by the following methods :

Element	Method	Process	Formula
Carbon and Hydrogen	Leibig's combustion method	A known weight of the organic compound (w g) is combusted with excess of O_2 and amount of CO_2 and H_2O formed are used to determine percentage of C and H. $\text{C}_x\text{H}_y + \left(x + \frac{y}{4}\right)\text{O}_2 \xrightarrow{\Delta} x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O}$	(i) $\text{C} \longrightarrow \text{CO}_2$ $\frac{12 \text{ g}}{44 \text{ g}}$ $\% \text{C} = \frac{12 \times \text{wt. of } \text{CO}_2 \times 100}{44 \times w}$ (ii) $2\text{H} \longrightarrow \text{H}_2\text{O}$ $\frac{2 \text{ g}}{18 \text{ g}}$ $\% \text{H} = \frac{2 \times \text{wt. of } \text{H}_2\text{O} \times 100}{18 \times w}$

Nitrogen	(i) Dumas method	<p>Elemental nitrogen in organic compound (w g) is converted into molecular nitrogen by suitable chemical method and its volume is changed to S.T.P. data.</p> $C_xH_yN_z + \left(2x + \frac{y}{2}\right)CuO \xrightarrow{\Delta} xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x + \frac{y}{2}\right)Cu$	$2N \longrightarrow N_2(g)$ $\frac{28 \text{ g}}{22.4 \text{ L at S.T.P.}}$ $\%N = \frac{28 \times V \times 100}{22.4 \times w}$ <p>where V is the volume of N_2 gas in L at S.T.P</p>
	(ii) Kjeldahl's method	<p>Nitrogen in the organic compound (w g) is converted into NH_3 by suitable chemical method which, in turn, is absorbed by V_1 mL of N_1 H_2SO_4.</p> $\text{Organic compound} \xrightarrow[\Delta]{H_2SO_4} (NH_4)_2SO_4 \xrightarrow[\Delta]{2NaOH} 2NH_3 \xrightarrow{H_2SO_4} (NH_4)_2SO_4$	$2N \longrightarrow NH_3 \approx H_2SO_4$ $\%N = \frac{1.4 \times N_1 \times V_1}{w}$
Sulphur	Carius method	<p>Sulphur in the organic compound (w g) is converted into H_2SO_4 by boiling with conc. HNO_3 and is precipitated as $BaSO_4$.</p> $S \xrightarrow[(ii) BaCl_2]{(i) HNO_3, \Delta} BaSO_4 \downarrow \text{white ppt.}$	$S \longrightarrow H_2SO_4 \longrightarrow BaSO_4$ $\frac{32 \text{ g}}{233 \text{ g}}$ $\%S = \frac{32 \times \text{wt. of } BaSO_4 \times 100}{233 \times w}$
Halogen	Carius method	<p>Halogen in the organic compound (w g) is precipitated as silver halide by boiling with conc. HNO_3 and then adding $AgNO_3$.</p>	<p>(i) $Cl \longrightarrow AgCl$ $\frac{35.5 \text{ g}}{143.5 \text{ g}}$ $\%Cl = \frac{35.5 \times \text{wt. of } AgCl \times 100}{143.5 \times w}$</p> <p>(ii) $Br \longrightarrow AgBr$ $\frac{80 \text{ g}}{188 \text{ g}}$ $\%Br = \frac{80 \times \text{wt. of } AgBr \times 100}{188 \times w}$</p> <p>(iii) $I \longrightarrow AgI$ $\frac{127 \text{ g}}{235 \text{ g}}$ $\%I = \frac{127 \times \text{wt. of } AgI \times 100}{235 \times w}$</p>
Phosphorus	Ignition method	<p>Phosphorus in organic compound (w g) is precipitated as magnesium ammonium phosphate by sequential reaction with nitric acid, $MgCl_2$ and mixture of $NH_4Cl + NH_4OH$ and then the precipitate is ignited to form magnesium pyrophosphate.</p>	$Mg_2P_2O_7 \longrightarrow 2P$ $\frac{222 \text{ g}}{62 \text{ g}}$ $\%P = \frac{\text{Mass of Phosphorus}}{\text{Mass of organic compound}} \times 100$ $= \frac{62 \times \text{wt. of } Mg_2P_2O_7 \times 100}{222 \times w}$
Oxygen			$\%O = 100 - \text{Sum of the percentages of other elements}$

SELF CHECK

- In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of $AgBr$. The percentage of bromine in the compound is (at. mass $Ag = 108$; $Br = 80$)
 - 48
 - 60
 - 24
 - 36
- 1.4 g of an organic compound was digested according to Kjeldahl's method and the ammonia evolved was absorbed in 60 mL of $M/10$ H_2SO_4 solution. The excess sulphuric acid required 20 mL of $M/10$ $NaOH$ solution for neutralisation. The percentage of nitrogen in the compound is
 - 3
 - 5
 - 10
 - 24

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Calculation of Empirical and Molecular Formula

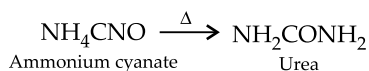
- ❑ **Empirical formula** : It is the simplest whole number ratio between the atoms of the various elements present in one molecule of the substance.
- ❑ **Molecular formula** : It gives the actual number of atoms of each element present in one molecule of the substance.
- ❑ Molecular formula = $n \times$ Empirical formula where, n is an integer (1, 2, 3, etc.)

SOME BASIC PRINCIPLES OF ORGANIC CHEMISTRY

- Introduction
- Nomenclature
- Isomerism
- Electronic Displacement in a Covalent Bond
- Types of Organic Reactions

TIPS TO REMEMBER

- ❑ Berzelius, a Swedish chemist proposed that a 'vital force' is responsible for the formation of organic compounds.
- ❑ This was rejected by F. Wohler who synthesised first organic compound urea from an inorganic compound.



- ❑ Acetic acid was synthesised by Kolbe and methane by Berthelot.

- ❑ **Tetravalency of carbon** : Carbon atom has four half filled orbitals in its excited state and hence forms four covalent bonds.

- ❑ **Shape and hybridisation** :

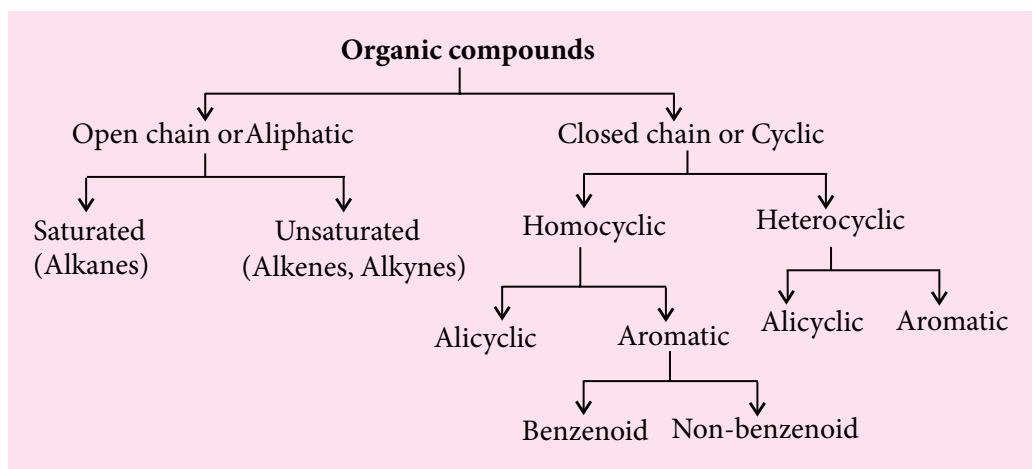
Hybridisation	Structure and bond angle	Examples
sp^3	Tetrahedral, $109^\circ 28'$	Ethane, methane
sp^2	Trigonal planar, 120°	Ethene, propene
sp	Linear, 180°	Ethyne, propyne

KEY POINT

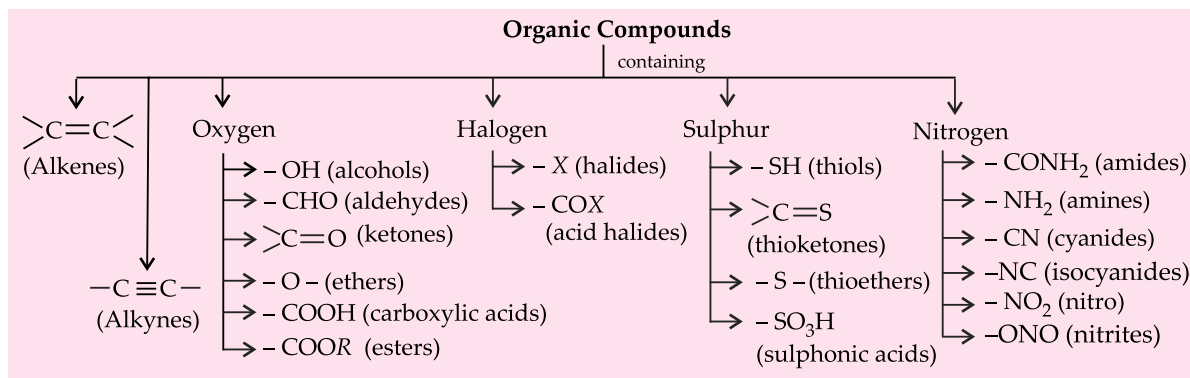
- Stability of a bond formed by a hybrid orbital is more than that formed by an unhybridised orbital.
- Greater the s -character of a hybrid orbital, lower is its energy. Hence the order of energies of various orbitals is $sp^3 > sp^2 > sp > s$.
- Greater the s -character of a hybrid orbital, smaller is its size. Therefore, the relative sizes of the hybrid orbitals follow the order $sp^3 > sp^2 > sp$.
- As expected from the size of the hybrid orbitals, sp -orbital forms the shortest and sp^3 orbital forms the longest bond.

Classification of Organic Compounds

- ❑ **Based on structure** :



❑ **Based on functional groups :**



Homologous Series

- ❑ A series of organic compounds each containing a characteristic functional group forms a homologous series in which each successive member differs by a —CH_2 group or by $12 + 2 \times 1 = 14$ mass units.

The members of the series are called *homologues* and the phenomenon is called *homology*.

IUPAC Nomenclature

- ❑ The five parts are described as follows :

- ❑ IUPAC name = 2° prefix + 1° prefix + word root + 1° suffix + 2° suffix

Word root	1° prefix	2° prefix	1° suffix	2° suffix
It denotes the number of carbon atoms present in the principal chain of the compound. C_1 -meth, C_2 -eth, C_3 -prop and C_4 -but. These are the special names for first four carbons.	It is used to differentiate between cyclic and acyclic compounds.	Some functional groups are not considered as functional groups but are treated as substituents which are denoted by secondary prefixes. <i>e.g.</i> , Fluoro —F ; Chloro —Cl ; Nitro —NO_2	It is always added to the word root to indicate whether carbon chain is saturated or unsaturated.	It is added to indicate a particular functional group present in the principal chain. <i>e.g.</i> , alcohols, acids, acid derivatives etc.

❑ **IUPAC rules for nomenclature of hydrocarbons :**

- *Parent chain rule* : From structure, the longest possible chain of C-atoms is chosen, this is called as parent chain. Accordingly, the appropriate root word is fixed.
- *Lowest number rule* : Once the parent chain is selected, the carbon atoms are numbered starting from the end that gives the lowest possible number to the carbon bearing substituent.
- *Lowest set of locants rule* : When more than one substituent is present, carbon atoms

bearing substituents should be numbered in such a way that there is least difference between them *i.e.*, that set of locants is preferred which has a lower number at the first point of difference.

❑ **IUPAC nomenclature of compounds with polyfunctional groups :**

- If more than one functional groups are present then one functional group is treated as the principal functional group (secondary suffix) and the remaining functional groups are treated as substituents (prefixes).

Class	Group	Suffix (if present as a functional group)	Prefix (if present as a substituent)
Carboxylic acids	—COOH	-oic acid	Carboxy
Sulphonic acids	—SO ₃ H	sulphonic acid	Sulpho
Esters	—COOR	alkyl alkanoate	Alkoxy carbonyl
Acyl halides	—COX	-oyl halide	Halocarbonyl
Amides	—CONH ₂	-amide	Carbamoyl
Nitriles	—C≡N	nitrile	Cyano
Isocyanides	—NC	isocyanide	Isocyano
Aldehydes	—CHO	-al	Formyl
Ketones	—CO—	-one	Oxo
Alcohols	—OH	-ol	Hydroxy
Thiols	—SH	-thiol	Sulphanyl
Amines	—NH ₂	amine	Amino
Imines	=NH	imine	Imino
Ethers	—O—	Alkoxy alkane	Alkoxy
Alkenes	>C=C<	-ene	Alkenyl
Alkynes	—C≡C—	-yne	Alkynyl
Halides	—X	—	Halo
Nitro	—NO ₂	—	Nitro
Alkanes		-ane	Alkyl

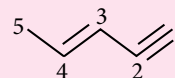
❑ **IUPAC nomenclature of aromatic compounds :**

- For substituted benzene compounds, the substituent is placed as prefix to the word benzene.
- In disubstituted benzene ring, the substituents are located at the lowest numbers possible while numbering the carbon atoms of the ring.
- In the trivial system of nomenclature, the prefix *ortho* (*o*-) indicates 1,2-, *meta* (*m*-) indicates 1,3- and *para* (*p*-) indicates 1,4-disubstituted benzene ring.
- In case of tri- or higher substituted benzene derivatives, common name of benzene derivatives is taken as the base compound. Number 1 position is assigned to the substituent of the base compound and lowest locant rule is followed for other substituents.

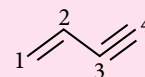
- Benzene ring is considered as substituent [Phenyl (Ph), —C₆H₅] when it is attached to an alkane with a functional group.

KEY POINT

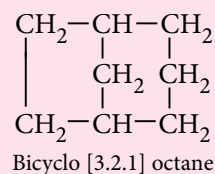
- Sometimes two equally long chains (but having different number of side chains) appear to be possible. In such cases, the chain which carries the larger number of side chains is the parent chain.
- Certain functional groups containing carbon as a part of the group (such as —CHO, —COOH, —COOR, —COCl and —CN) can be present only at one end of the chain. For such groups known as *chain terminating groups*, the numbering of the parent chain is always started from the carbon of this group. Therefore, such functional groups always get number 1 and this number need not be mentioned while writing the name of the compound.
- If the principal chain contains two or more multiple bonds, the numbering is done in accordance with lowest set of locants rule.



- If both double and triple bonds are present in the parent chain and numbering of parent chain from any end gives the same set of locants, then numbering is done from the end which gives the lowest locant to the double bond.

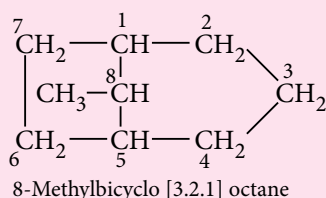


- Bicyclic compounds are named by adding prefix bicyclo to the name of hydrocarbon corresponding to total number of carbon atoms in two rings. In between the words bicyclo and alkane an expression in the square brackets is placed that represents the number of carbon atoms in each bridge connecting two bridge heads, in descending order separated from one another by full stop.



KEY POINT

- If substituent is present, we number the bridged ring system beginning at one bridge head, proceeding first along the longest bridge to the other bridge head, then along the next longest bridge back to the first bridge head. The shortest bridge is numbered last.



Isomerism

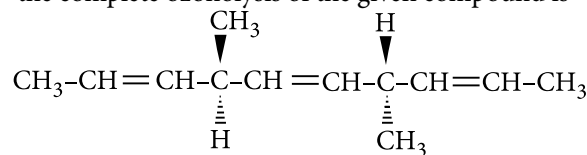
- The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as *isomerism*.

Types of structural isomerism :

Isomerism	Description	Examples
Chain isomerism	Arises due to different arrangements of carbon atoms leading to linear and branched chains. The chain isomers have almost similar chemical properties but different physical properties.	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$, $\text{H}_3\text{C}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$ Butane Iso-butane
Position isomerism	Arises due to different positions of side chains, substituents, functional groups, double bonds, triple bonds, etc. on the parent chain.	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_3$, But-1-ene $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_3$ But-2-ene
Functional isomerism	Arises due to presence of different functional groups. The functional isomers have the same molecular formula but possess different functional groups. The functional isomers show different physical as well as chemical properties.	$\text{H}_3\text{C}-\text{CH}_2-\text{OH}$, $\text{H}_3\text{C}-\text{O}-\text{CH}_3$ Ethyl alcohol Dimethyl ether
Metamerism	Arises when different alkyl groups are attached to the same functional group.	$\text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$ Diethyl ether or Ethoxyethane $\text{H}_3\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ Methyl propyl ether or 1-Methoxypropane
Tautomerism	Refers to the dynamic equilibrium between two compounds with same molecular formula. It is also called as <i>desmotropism</i> or <i>kryptotropism</i> or <i>prototropy</i> or <i>allelo-tropism</i> . In general, the tautomers have different functional groups and exist in dynamic equilibrium with each other due to a rapid interconversion from one form to another.	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $\text{H}_3\text{C}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_3$ Acetone (keto form) </div> \rightleftharpoons <div style="text-align: center;"> $\text{H}_3\text{C}-\overset{\text{OH}}{\underset{\text{ }}{\text{C}}}=\text{CH}_2$ Prop-1-en-2-ol (enol form) </div> </div> <p style="text-align: center;">Keto-enol tautomerism</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $\text{H}_3\text{C}-\overset{\text{O}}{\underset{\text{ }}{\text{N}}}-\text{O}$ Nitromethane (nitro-form) </div> \rightleftharpoons <div style="text-align: center;"> $\text{H}_2\text{C}=\overset{\text{OH}}{\underset{\text{ }}{\text{N}}}-\text{O}$ (aci-form) </div> </div> <p style="text-align: center;">Nitro-aci tautomerism</p>

SELF CHECK

3. The number of optically active products obtained from the complete ozonolysis of the given compound is



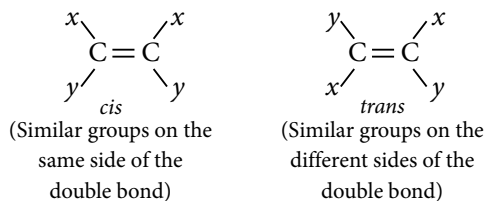
- (a) 0 (b) 1
(c) 2 (d) 4 (JEE Advanced 2012)

4. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is(are)

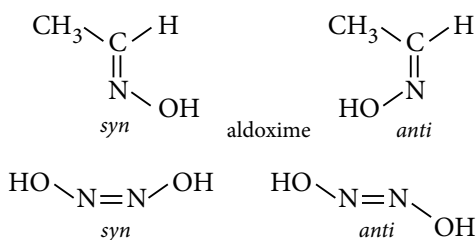
- (a) sp and sp^3 (b) sp and sp^2
(c) only sp^2 (d) sp^2 and sp^3
(JEE Advanced 2012)

Types of stereoisomerism :

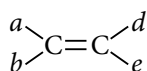
- **Geometrical isomerism** : Geometrical isomers have the same structural formula but they differ in the spatial arrangement of atoms or groups of atoms about double bond ($C=C$, $C=N$ or $N=N$).



- In addition to alkenes, compounds containing $C=N$ (aldoxime and ketoxime) and $N=N$ (azo compounds) bonds also show geometrical isomerism. However, in these cases, 'syn' (for *cis*) and 'anti' (for *trans*) are more commonly used.

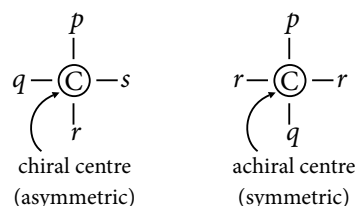


- **E and Z system of nomenclature** : For highly substituted alkenes having four different atoms or groups attached to $C=C$ bond, *cis* and *trans* designations cannot be used. In such cases, *E-Z* notation is used.



- *E* is assigned to an isomer in which high priority atoms or groups are on the opposite sides.
- *Z* is assigned to an isomer in which high priority atoms or groups are on the same side.
- In polyenes number of geometrical isomers = 2^n where, n is the number of double bonds.
- **Optical isomerism** : Compounds having similar physical and chemical properties but differing only in the behaviour towards polarised light are called *optical isomers* and the phenomenon is called optical isomerism.

- Some substances have the ability to rotate the plane polarised light either to the right (clockwise) or to the left (anticlockwise). These substances are termed as *optically active* substances and the property is called *optical activity*.
- In order to exhibit optical activity, an object must be *chiral*.
- The compound is said to have *chirality* if the central carbon atom is attached to four different groups and this centre is called *chiral (asymmetric) centre* or *stereogenic centre* or *stereocentre*.



- If molecule has a plane of symmetry it is *achiral* and if molecule has no plane of symmetry it is *chiral*.
- **Enantiomers** or *d and l isomers* are the optical isomers which are non-superimposable mirror images (or dissymmetric).
- **Diastereomers** are the optical isomers which are not mirror images of each other. They have different physical properties and magnitude of specific rotation.
- **Meso compounds** are those compounds which have two or more even number of chiral carbon atoms and have an internal plane of symmetry. They are optically inactive due to *internal compensation*.

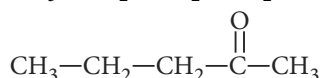
KEY POINT

- Terminal alkenes like propene isobutylene, 2, 3-dimethylbutene do not show geometrical isomerism.
- Geometrical isomers are also called configurational isomers as they have fixed configuration.
- **Auwer – Sketa Rule** : This is an empirical rule according to which out of a pair of geometrical isomers (*cis* and *trans*) the *cis* isomers has higher b.pt., density and refractive index.

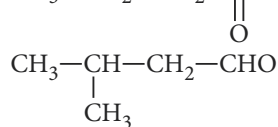
SELF CHECK

5. Which of the following compounds will exhibit geometrical isomerism?
 (a) 2-Phenyl-1-butene
 (b) 1, 1-Diphenyl-1-propane
 (c) 1-Phenyl-2-butene
 (d) 3-Phenyl-1-butene (JEE Main 2015)
6. Which of the following pairs of compounds are positional isomers?

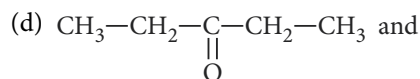
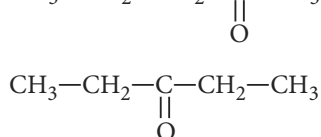
- (a) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CHO}$ and



- (b) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—CH}_3$ and



- (c) $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—CH}_3$ and



7. The number of structural isomers for C_6H_{14} is
 (a) 3 (b) 4
 (c) 5 (d) 6 (JEE Main 2015)

Electronic Displacement in a Covalent Bond

□ Fission of a covalent bond :

- *Heterolytic cleavage* involves breaking of a covalent bond in such a fashion that the shared pair of electrons remains with one of the fragments, which results in the formation of carbocations or carbanions as intermediates.
- *Homolytic cleavage* involves breaking of a covalent bond in such a fashion that one of the electrons of the shared pair goes with each of the bonded atom, which results in the formation of free radicals as intermediates.

□ Reaction intermediates :

Intermediates	Definition	Hybridisation of carbon and shape	Stability order
Carbocation	Carbon species carrying +ve charge on carbon.	sp^2 hybridised carbon and planar structure.	$3^\circ > 2^\circ > 1^\circ$
Carbanion	Carbon species carrying -ve charge on carbon.	sp^3 hybridised carbon and pyramidal shape.	$1^\circ > 2^\circ > 3^\circ$
Free radical	Atom or group of atoms having odd or unpaired electron.	sp^2 hybridised carbon and planar structure.	$3^\circ > 2^\circ > 1^\circ$

□ Attacking reagents :

Reagent	Description	Examples
Electrophiles	They are positively charged or neutral molecules having electron deficient atom, seeking a site of high electron density. Electrophiles have an incomplete outer shell and are also called <i>Lewis acids</i> (electron-pair acceptors).	Charged : H_3O^+ , X^+ (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$), NO_2^+ , NO^+ , NH_4^+ , SO_3^+ , $\text{C}_6\text{H}_5\text{N}_2^+$, R^+ , RCO^+ . Neutral : BF_3 , AlCl_3 , FeCl_3 , SiCl_4 , BeCl_2 , ZnCl_2 , SO_3 , CO_2 , CS_2 , CX_4 , RCOCl , $>\text{C}=\text{O}$, $:\text{CCl}_2$.

Nucleophiles	They are negatively charged or neutral molecules having electron-rich atom with unshared electron pair, seeking electron deficient site to attack. They are also called <i>Lewis bases</i> (electron-pair donors).	Charged : H^- , OH^- , X^- , CN^- , N_3^- , RO^- , R^- , RS^- , SH^- , HSO_3^- , NO_2^- , NH_2^- , RCOO^- , $\text{HC}\equiv\text{C}^-$. Neutral : $\ddot{\text{N}}\text{H}_3$, $\text{H}_2\ddot{\text{O}}$, $\text{R}\ddot{\text{O}}\text{H}$, $\text{R}\ddot{\text{O}}\text{R}$, $\text{R}\ddot{\text{S}}\text{H}$, RMgX , $\text{Ph}_3\ddot{\text{P}}$, RLi , LiAlH_4 , etc.
Ambiphiles (ambident)	They behave like both electrophiles and nucleophiles hence, have dual nature (amphoteric).	Charged : H_3O^+ Neutral : $\text{R}\ddot{\text{O}}\text{H}$, $\text{H}\ddot{\text{O}}\text{H}$ and RPH_2

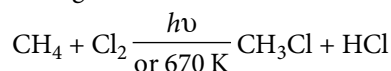
□ Electron displacement effects in covalent bonds :

- **Inductive effect** : Displacement of σ electrons along a saturated carbon chain when an electron donating (+I effect) or electron withdrawing (−I effect) group is attached at the end of the carbon chain.
 - Decreasing order of −I effect : $-\text{NO}_2 > -\text{CN} > -\text{COOH} > -\text{F} > -\text{Cl} > -\text{Br} > -\text{I} > -\text{H}$
 - Decreasing order of +I effect : $(\text{CH}_3)_3\text{C}- > (\text{CH}_3)_2\text{CH}- > \text{CH}_3\text{CH}_2- > \text{CH}_3- > \text{D}- > \text{H}-$
- **Electromeric effect** : It involves complete transfer of π electrons of a multiple bond towards one of the bonded atoms in the presence of an attacking reagent.
 - +E effect : When electron transfer takes place towards the atom to which the attacking reagent gets attached.
 - −E effect : When electron transfer takes place away from the atom to which the attacking reagent gets attached.
- **Resonance or Mesomeric effect** : It is defined as the polarity produced in the molecule by the interaction of two π bonds or between a π bond and a lone pair of electrons present on adjacent atom.
 - +R or +M effect : $-\text{OH}$, $-\text{OR}$, $-\text{SH}$, $-\text{SR}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, etc.
 - −R or −M effect : $>\text{C}=\text{O}$, $-\text{CHO}$, $-\text{COOR}$, $-\text{CN}$, $-\text{NO}_2$, etc.
- **Hyperconjugation** : It involves delocalisation of σ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared *p*-orbital. For an alkyl group attached to unsaturated system it decreases with decrease in number of α -hydrogens :
 $\text{CH}_3- > \text{CH}_3\text{CH}_2- > (\text{CH}_3)_2\text{CH}- > (\text{CH}_3)_3\text{C}-$

Types of Organic Reactions

- **Substitution reactions (or displacement reactions)** : These are further classified into three types :

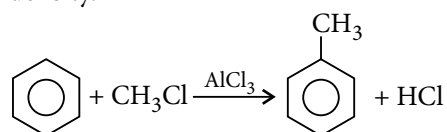
- **Free radical substitution reaction** takes place through free radical intermediates, e.g.,



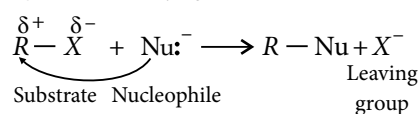
(Here, Cl^\bullet is formed as reaction intermediate)

- **Electrophilic substitution reaction (S_E)** involves the attack by an electrophile. It is of two types :

- **Unimolecular (S_{E1})** is first order reaction. These reactions are very rare and generally takes place in aliphatic compounds, e.g.,
 $\text{CH}_3\text{CH}_2\text{MgBr} + \text{HBr} \longrightarrow \text{CH}_3\text{CH}_3 + \text{MgBr}_2$
- **Bimolecular (S_{E2})** is second order reaction and very common in aromatic compounds where π -electrons of benzene ring are highly delocalised and an electrophile can attack this region of high electron density.



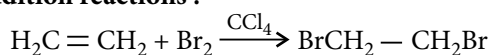
- **Nucleophilic substitution reactions (S_N)** are those reactions in which a stronger nucleophile displaces a weaker nucleophile and the atom or group which departs with its bonding pair of electrons is called the *leaving group* (or *nucleofuge*).



- Better the leaving group, more facile is the reaction. It is of two types :

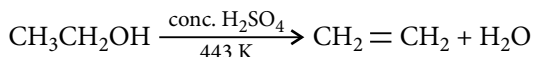
Unimolecular (S_N1)	Bimolecular (S_N2)
It is first order reaction.	It is second order reaction.
Generally carried out in polar protic solvents like water, alcohol and acetic acid.	Carried out in polar aprotic solvents like acetone, DMSO, acetonitrile, or DMF.
Takes place in two steps through carbocation as the intermediate.	Takes place in one step through transition state.
Rate of reaction : $3^\circ > 2^\circ > 1^\circ > \overset{+}{\text{CH}_3}$ (fastest) (slowest) Greater the stability of carbocation, faster will be the reaction.	Rate of reaction : $\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$ halides (fastest) (slowest) Lesser the steric hindrance in transition state, faster will be the reaction.
Tends to proceed with weak nucleophiles <i>e.g.</i> ; CH_3OH , H_2O , $\text{CH}_3\text{CH}_2\text{OH}$, etc.	Tends to proceed with strong nucleophiles, <i>e.g.</i> ; CH_3O^- , CN^- , OH^- , etc.
Configuration is retained but in front attack inversion takes place (racemisation and inversion).	Inversion of configuration takes place (<i>Walden inversion</i>).

□ **Addition reactions :**

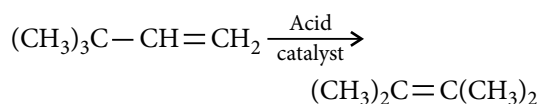


These are also of three types like substitution reactions : Electrophilic addition, Nucleophilic addition and Free radical addition reactions.

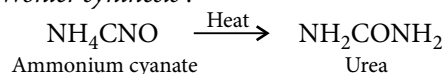
- **Elimination reactions :** These are opposite of addition reactions in which two atoms or groups of atoms are lost to form compounds with double and triple bonds, *e.g.*;



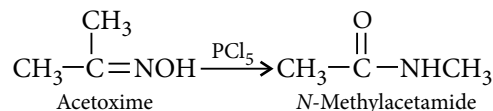
- These are of three types : Unimolecular elimination ($E1$), Unimolecular conjugate base elimination ($E1cb$) and Bimolecular elimination ($E2$) reactions.
- **Rearrangement reactions :** These reactions involve reorganisation of the constituent parts of a molecule. In these, functional groups, double bonds, H atoms or alkyl groups are moved from one C atom to another, *e.g.*;



○ **Wöhler synthesis :**



○ **Beckmann rearrangement :**



KEY POINT

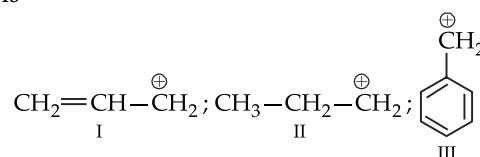
- Relative stabilities of carbocations follow the order :
 – benzylic $\sim 3^\circ > \text{allylic} \sim 2^\circ > 1^\circ > \overset{+}{\text{CH}_3}$
- Relative stabilities of carbanions follow the order :
 aromatic $> \text{benzyl} > \text{allyl} > \text{HC} \equiv \bar{\text{C}} > \text{H}_2\text{C} = \bar{\text{C}} > \bar{\text{C}}\text{H}_3 > \text{CH}_3\bar{\text{C}}\text{H}_2 > (\text{CH}_3)_2\bar{\text{C}}\text{H} > (\text{CH}_3)_3\bar{\text{C}}$

1°
 2°
 3°
- Relative stabilities of free radicals follow the order :
 $\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2 > \text{CH}_2=\text{CH}\dot{\text{C}}\text{H}_2 > (\text{CH}_3)_3\dot{\text{C}} > (\text{CH}_3)_2\dot{\text{C}}\text{H} > \text{CH}_3\dot{\text{C}}\text{H}_2 > \dot{\text{C}}\text{H}_3$

(Benzyl)
(Allyl)
 3°
 2°
 1°

SELF CHECK

8. The order of stability of the following carbocations is



- (a) III > I > II (b) III > II > I
 (c) II > III > I (d) I > II > III
- (JEE Main 2013)

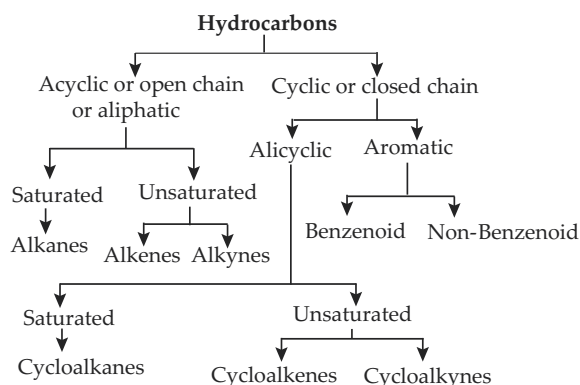
HYDROCARBONS

- Classification • Alkanes
- Alkenes • Alkynes
- Aromatic Hydrocarbons

TIPS TO REMEMBER

- Organic compounds composed of only carbon and hydrogen are called *hydrocarbons*.

Classification



Alkanes

- The saturated hydrocarbons are represented by the general formula C_nH_{2n+2} .

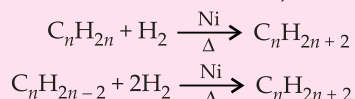
General properties :

- The normal alkanes are colourless gases (C_1 to C_4), colourless liquids (C_5 to C_{17}) and from C_{18} onwards colourless solids.
- As branching increases, melting and boiling points decrease. The boiling point increases steadily with increase in molecular mass.
- Density of alkanes also increases with size of the molecule.
- They are generally insoluble in polar solvents like water but soluble in non-polar solvents like ether, chloroform, etc.

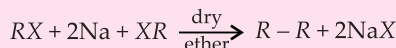
Methods of preparation

1. By hydrogenation of unsaturated hydrocarbons

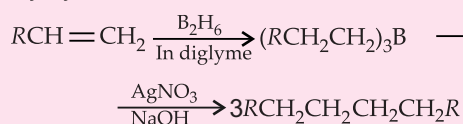
(Sabatier & Senderen's reaction) :



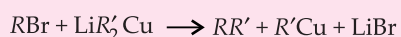
2. Wurtz reaction :



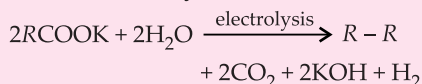
3. By hydroboration of alkenes :



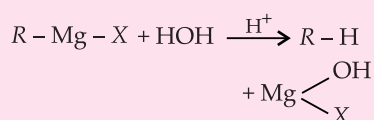
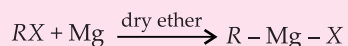
4. Corey-House synthesis :



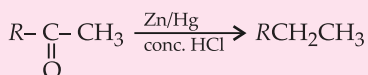
5. Kolbe's electrolysis :



6. From Grignard's reagent :

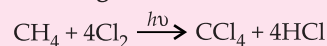


7. From carbonyl compounds (Clemmensen reduction) :

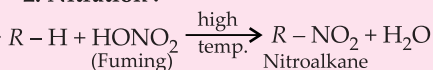


Chemical properties

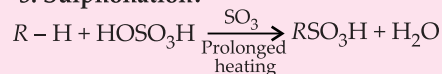
1. Halogenation :



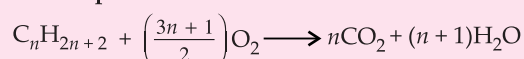
2. Nitration :



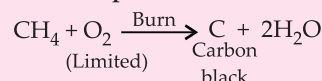
3. Sulphonation :



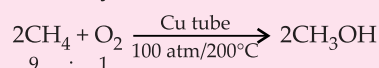
4. Complete combustion :



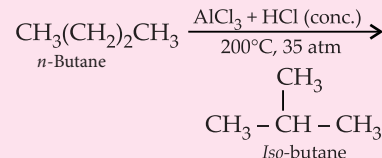
5. Incomplete combustion :



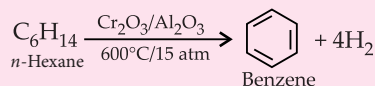
6. Catalytic oxidation :



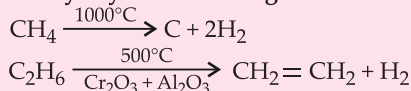
7. Isomerisation :



8. Aromatisation :

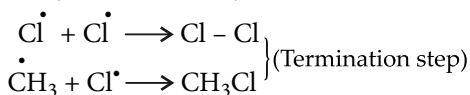
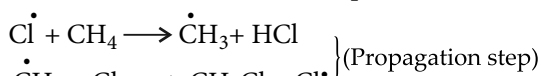
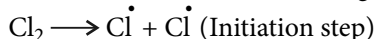


9. Pyrolysis or cracking :



ALKANES

- ❑ **Mechanism of halogenation :** The mechanism is believed to involve the following steps :

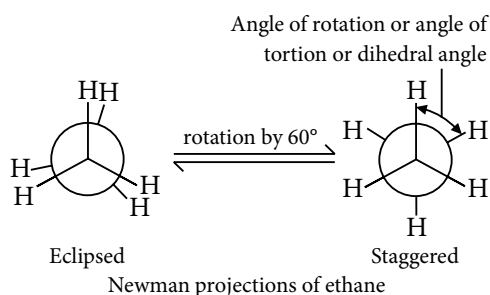
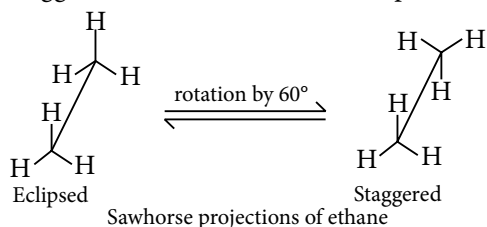


Reactivity of halogens : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

Reactivity of hydrogen : $3^\circ > 2^\circ > 1^\circ$

- ❑ **Conformations of Ethane (Sawhorse and Newman Projections)**

- **Staggered conformation :** The hydrogen atoms attached to two carbons are far apart and experience minimum repulsion.
- **Eclipsed conformation :** The hydrogen atoms attached to two carbons are as close together as possible and experience maximum repulsion.
- **Gauche or Skew form :** A rotation of 60° converts a staggered conformation into an eclipsed conformation, or *vice-versa*. Rotation between 0° to 60° generates one of the many other arrangements in between staggered and eclipsed forms. These arrangements are called *gauche* or *skew form*.
- **Order of stability :**
Staggered > Skew or Gauche > Eclipsed



KEY POINT

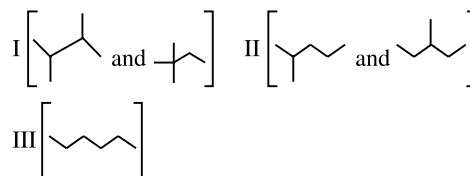
- Methane cannot be prepared by Kolbe's electrolytic method.
- Ethane is prepared in the laboratory by electrolysis of conc. aqueous solution of CH_3COOK .

KEY POINT

- Electrolysis of HCOONa gives H_2 gas at both cathode as well as anode.
- During chlorination the relative ease of abstraction of H atom is 1 : 3.8 : 5 for primary, secondary and tertiary hydrogen respectively.
- In bromination the ratio becomes 1 : 82 : 1600 for 1° , 2° and 3° H atoms. The yield of alkanes produced can be accordingly predicted.

SELF CHECK

9. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.



The correct order of their boiling point is

- (a) $\text{I} > \text{II} > \text{III}$ (b) $\text{III} > \text{II} > \text{I}$
(c) $\text{II} > \text{III} > \text{I}$ (d) $\text{III} > \text{I} > \text{II}$

(JEE Advanced 2014)

10. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO_2 . The empirical formula of the hydrocarbon is

- (a) C_7H_8 (b) C_2H_4
(c) C_3H_4 (d) C_6H_5

(JEE Main 2013)

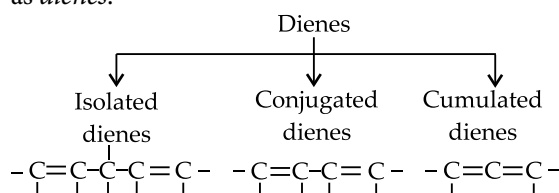
11. Which branched chain isomer of the hydrocarbon with molecular mass 72 u gives only one isomer of mono substituted alkyl halide?

- (a) Neopentane (b) Isohexane
(c) Neohexane (d) Tertiary butyl chloride

(JEE Main 2012)

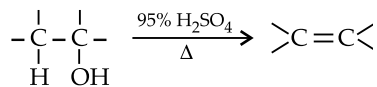
Alkenes

- ❑ Organic compounds containing $\text{C} = \text{C}$ are known as *alkenes*. Alkenes with two double bonds are known as *dienes*.



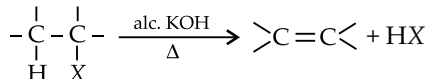
Methods of preparation :

- By dehydration of alcohols :

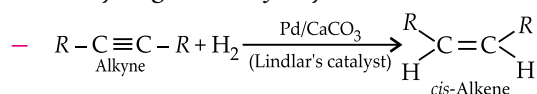


Saytzeff rule : If a single starting compound can yield two or more isomers then more substituted alkene is formed in greater amount.

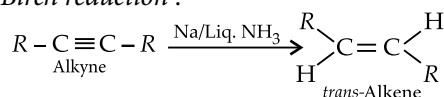
- By dehydrohalogenation of alkyl halides :



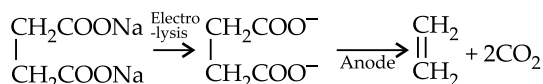
- Partial hydrogenation of alkynes :



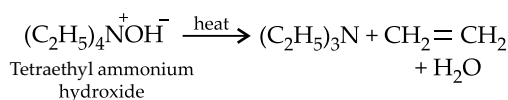
- Birch reduction :



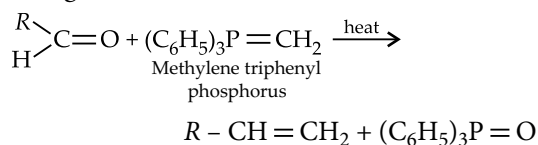
- Electrolysis of salt of dicarboxylic acids :



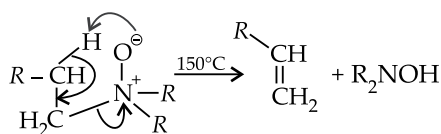
- Hofmann elimination :



- Wittig reaction :



- Cope reaction :

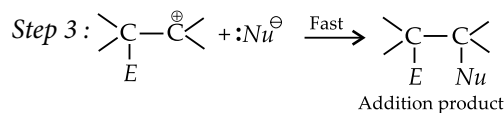
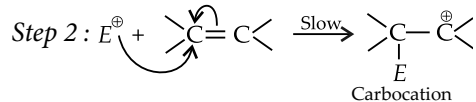
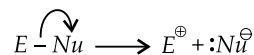


Properties :

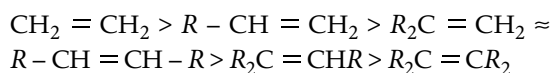
- All alkenes are colourless and odourless (except ethene). Ethene has pleasant odour.
- C₁ - C₃ (gases), C₄ - C₁₆ (liquids), C₁₇ onwards solids.
- Boiling point, melting point and specific densities increase with increase in molecular mass in homologous series.

- Mechanism of electrophilic addition :

Step 1 : The reagent ionises

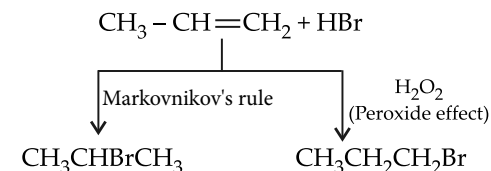


Reactivity order :

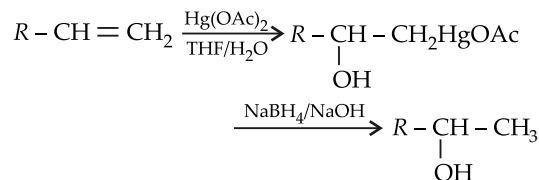


- Markovnikov's rule :** The negative part of unsymmetrical reagent adds to less hydrogenated carbon atom of double bond.

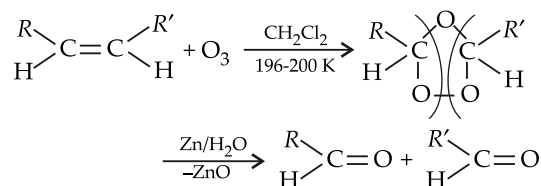
- Peroxide effect :** Addition of HBr in presence of peroxide gives products opposite to Markovnikov's rule.



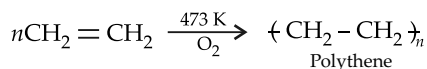
- Oxymercuration-demercuration :**



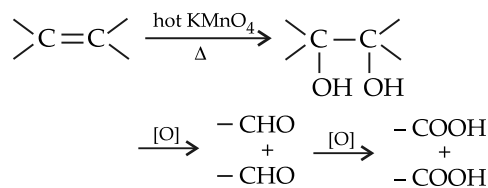
- Ozonolysis :**



- Polymerisation :**



- Oxidation :** Hot alkaline KMnO₄ or K₂Cr₂O₇ as oxidising agent.



CONCEPT MAP

STRUCTURE OF ATOM

Nearly all properties of matter can be explained in terms of atoms consisting of electrons, protons and neutrons and the various models given to describe the structure of atom are based on classical, quantum and wave mechanical concepts.

SUB-ATOMIC PARTICLES AND ATOMIC MODELS

Electrons

- Negatively charged material particles.
- Charge = $-1.6022 \times 10^{-19} \text{ C}$
- Mass = $9.10939 \times 10^{-31} \text{ kg}$
- Relative charge = -1

Protons

- Positively charged material particles.
- Charge = $+1.6022 \times 10^{-19} \text{ C}$
- Mass = $1.67262 \times 10^{-27} \text{ kg}$
- Relative charge = $+1$

Neutrons

- Electrically neutral particles.
- Charge = 0
- Mass = $1.67493 \times 10^{-27} \text{ kg}$

SUB-ATOMIC PARTICLES

Rutherford's Model

- An atom consists of a small positively charged nucleus and electrons revolve around it.
- Could not explain the stability of atom, line spectra of elements, distribution of electrons and energies of electrons.

Thomson Model

- An atom has a spherical shape in which the positive charge is uniformly distributed and electrons are embedded.
- Explained overall neutrality of the atom but could not explain the results of scattering experiments.

Bohr's Model

- Electrons revolve around the nucleus in certain definite orbits called stationary states having fixed energies.
- Electrons revolve only in those orbits for which the angular momentum is an integral multiple of $\frac{h}{2\pi}$.
- Radii of stationary states, $r_n = \frac{a_0 n^2}{Z}$
- Energies of different stationary states, $E_n = \frac{-1312}{n^2} Z^2 \text{ kJ mol}^{-1}$
- Velocity of electrons in n^{th} orbit, $v_n = 2.188 \times 10^8 \times \frac{Z}{n} \text{ cm s}^{-1}$
- No. of spectral lines = $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$
- Applicable only for one electron system.
- Does not explain Zeeman and Stark effects.

ATOMIC MODELS

ELECTRO- MAGNETIC RADIATIONS

Wave Nature of Electromagnetic Radiations

- Electrically charged particle under acceleration produces electromagnetic waves.
 $c = \nu \lambda$ and $\frac{1}{\lambda} = \bar{\nu}$
- *Electromagnetic spectrum* : Cosmic rays < γ -rays < X-rays < UV rays < Visible < Infrared < Micro waves < Radio waves (Increasing order of wavelength).

Particle Nature of Electromagnetic Radiations

- Particle nature explains the following phenomena:
 - *Black body radiation* : Radiation emitted by a black body.
 - *Photoelectric effect* : Emission of electrons from the surface of a metal when radiation of certain minimum frequency strikes the metal and the kinetic energy of ejected electron,

$$\frac{1}{2} m v^2 = h\nu - h\nu_0$$

Quantum Mechanical Model

- Based on the following two concepts:
 - *Heisenberg's uncertainty principle* : The exact position and exact momentum of an electron cannot be determined simultaneously.
- *Dual behaviour of matter* : All material particles possess wave as well as particle character and the wave associated with a particle is called *de-Broglie wave*.

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

QUANTUM NUMBERS

A set of four numbers which gives complete information about an electron.

Principal Quantum Number (n)

- Tells size and energy of an orbital.
- Maximum number of electrons in a shell is given by $2n^2$.

Azimuthal Quantum Number (l)

- Tells number of subshells and shape of orbitals.
- For a particular value of n ,
 $l = 0 \text{ to } (n - 1)$
- Shape of s -orbital is spherical, p -orbital is dumb-bell and that of d -orbital is double dumb-bell.

Magnetic Quantum Number (m_l)

- Tells number of orbitals present in any subshell.
- For a given value of l , it can have all the values ranging from $-l$ to $+l$ including zero.

Spin Quantum Number (s or m_s)

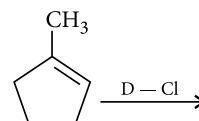
- Tells direction of electron spin and has value $+1/2$ or $-1/2$.

KEY POINT

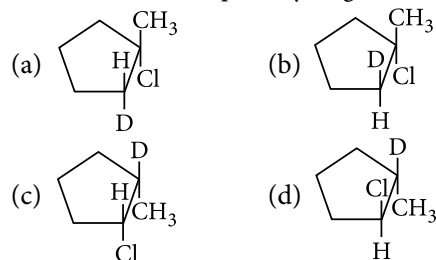
- In case of dialkyl derivatives of ethylene which exist as geometrical isomers, the *trans* isomer is more stable than the *cis* isomer. This is because of lesser crowding in *trans* isomers.
- With alkaline KMnO_4 ,
 =CH_2 part of alkene is oxidised to CO_2 and H_2O
 =CRR' part is oxidised to RCOR'
- N-Bromosuccinimide (NBS) is used for the bromination of alkenes at allylic position.
- $\text{RhCl}(\text{Ph}_3\text{P})_3$ is Wilkinson's catalyst and used for the hydrogenation of alkenes.

SELF CHECK

12. What is the major product expected from the following reaction?



Where D is an isotope of hydrogen.



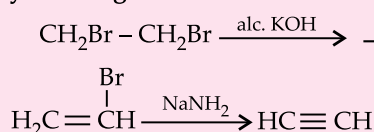
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Alkynes

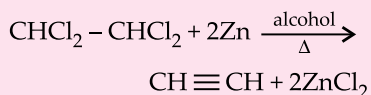
- Hydrocarbons with $\text{C}\equiv\text{C}$ are known as *alkynes*.

Methods of Preparation

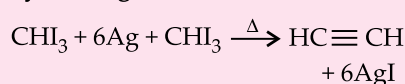
1. Dehydrohalogenation of dihalides :



2. By heating 1,1,2,2-tetrachloroethane with zinc :



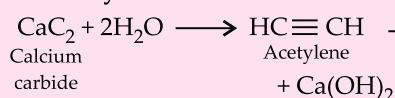
3. By heating iodoform with silver :



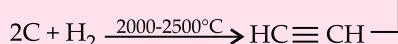
4. Kolbe's electrolysis :



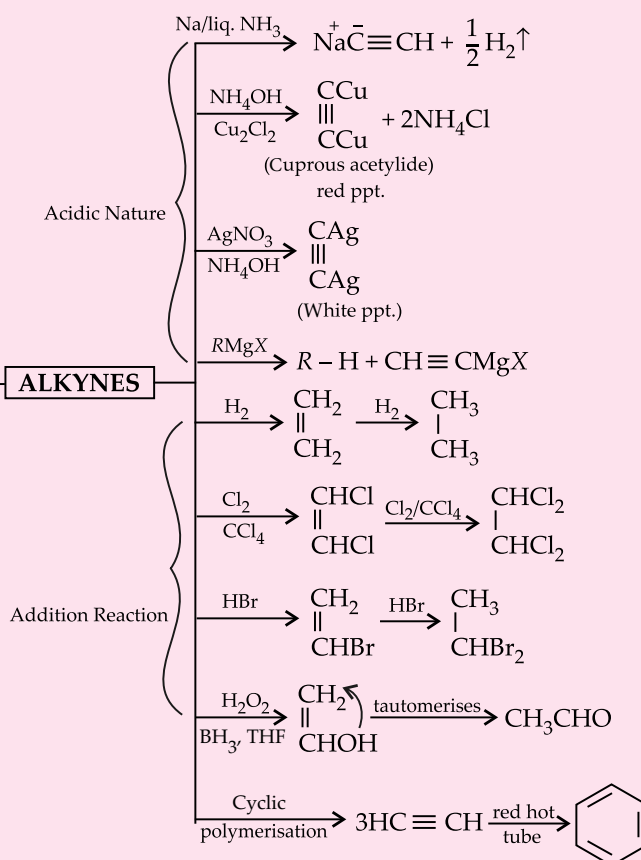
5. Laboratory method :



6. Berthelot synthesis :



Chemical Properties



- ❑ **Acidic nature :** Acetylene is acidic in nature. As s -character increases, acidic nature increases.

Hybridisation : $sp > sp^2 > sp^3$ (acidic nature)

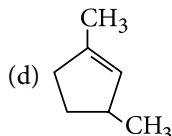
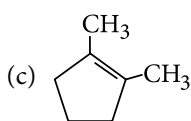
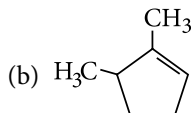
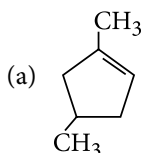
s -character : 50% 33.3% 25%

KEY POINT

- Alkaline KMnO_4 ($\text{MnO}_4^- + \text{OH}^-$) is known as *Baeyer's reagent* and used for test of unsaturation (glycol forms).
- Alkynes show chain, position and functional isomerism.
- Acetylene can undergo linear polymerisation by passing it through CH_2Cl_2 solution containing NH_4Cl . (Monovinyl acetylene and divinyl acetylene are formed).

SELF CHECK

13. Which compound would give 5-keto-2-methyl-hexanal upon ozonolysis?



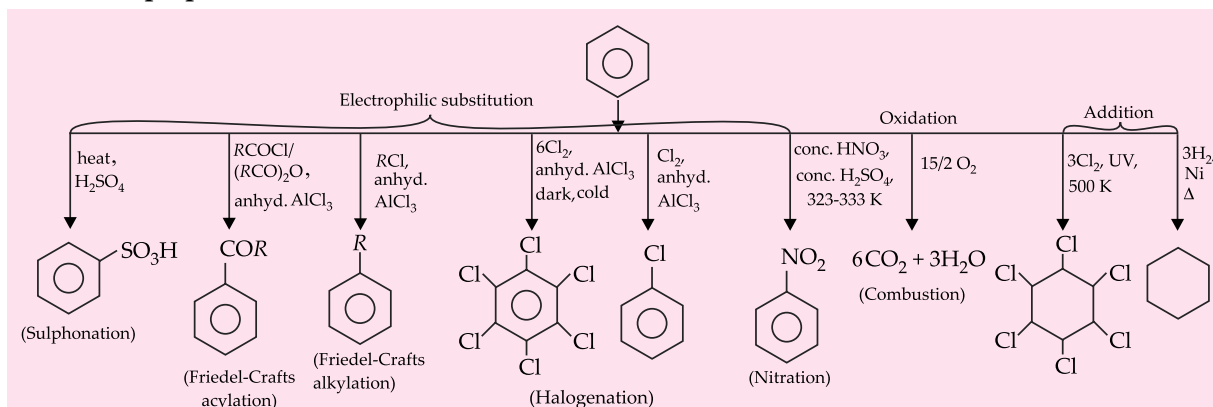
(JEE Main 2015)

Aromatic Hydrocarbons

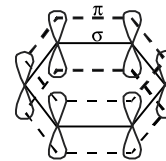
❑ Structure of benzene :

- All six carbon atoms in benzene are sp^2 hybridised.
- The sp^2 hybrid orbitals overlap with each other and with s -orbitals of the six hydrogen atoms forming C – C and C – H σ bonds respectively.

❑ Chemical properties :



- All σ -bonds in benzene lie in one plane and all bond angles are 120° .
- One half of π -molecular orbital lies above and the other half lies below the plane of the σ -bond.



- ❑ **Aromaticity (Huckel Rule) :** Huckel rule of aromaticity is applied to all the ring systems whether they have benzene ring or not and possess the following characteristics :

- Planarity
- Complete delocalisation of π -electrons in the ring.
- Presence of $(4n + 2)\pi$ -electrons in the ring where $n = 0, 1, 2, 3, \dots$

For example,



Benzene

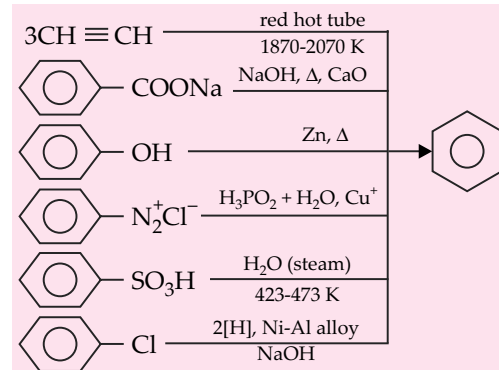


Cyclopentadienyl anion
($n = 1, 6 \pi$ electrons)



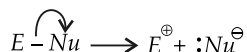
Cycloheptatrienyl cation

❑ Preparation :

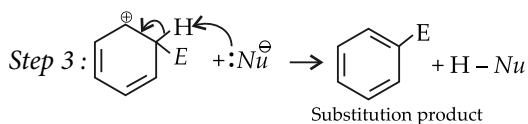
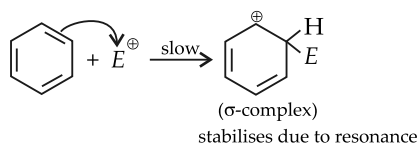


- ❑ **Mechanism of electrophilic substitution reactions:** Benzene undergoes substitution because it is an electron rich system due to delocalised π -electrons.

Step 1 : Formation of an electrophile

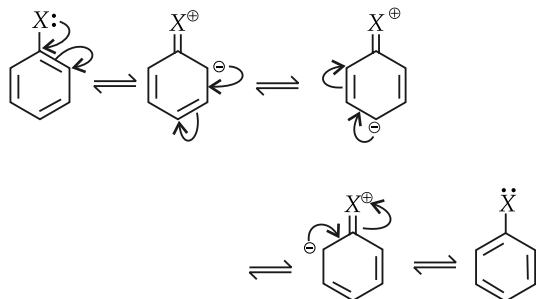


Step 2 : Electrophile attacks on aromatic ring to form σ -complex.



❑ **Directive influence :**

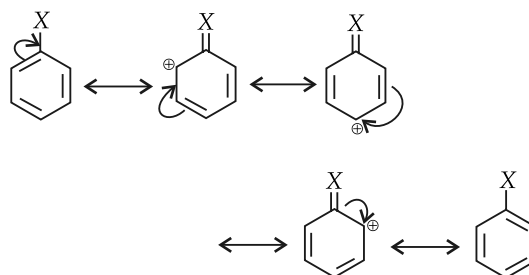
- Groups with positive mesomeric effect (+M) increases electron density at *o*- and *p*-positions due to delocalisation.



(here X may be - OH, - F, - Cl, - Br, - I.)

Thus, electrophile attacks on *o*- and *p*-positions because these are electron rich positions while nucleophile will attack on *m*-position because *m*-position is less electron rich.

- Groups with negative mesomeric effect (-M) decreases electron density on *o*- and *p*-positions, so electrophile will attack on *m*-position and nucleophile will attack on *o*- and *p*-positions.

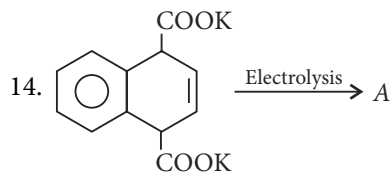


(here, X may be - NO₂, - SO₃H, - CN.)

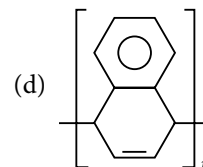
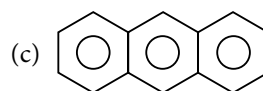
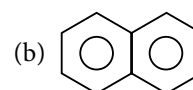
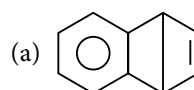
🔑 **KEY POINT**

- o*, *p*-directing groups also activate benzene ring towards further substitution while *meta*-directing groups deactivate benzene ring.
- Halogens are exception; they are *o*, *p*-directing but deactivating.

✅ **SELF CHECK**



A is



(JEE Main 2015)

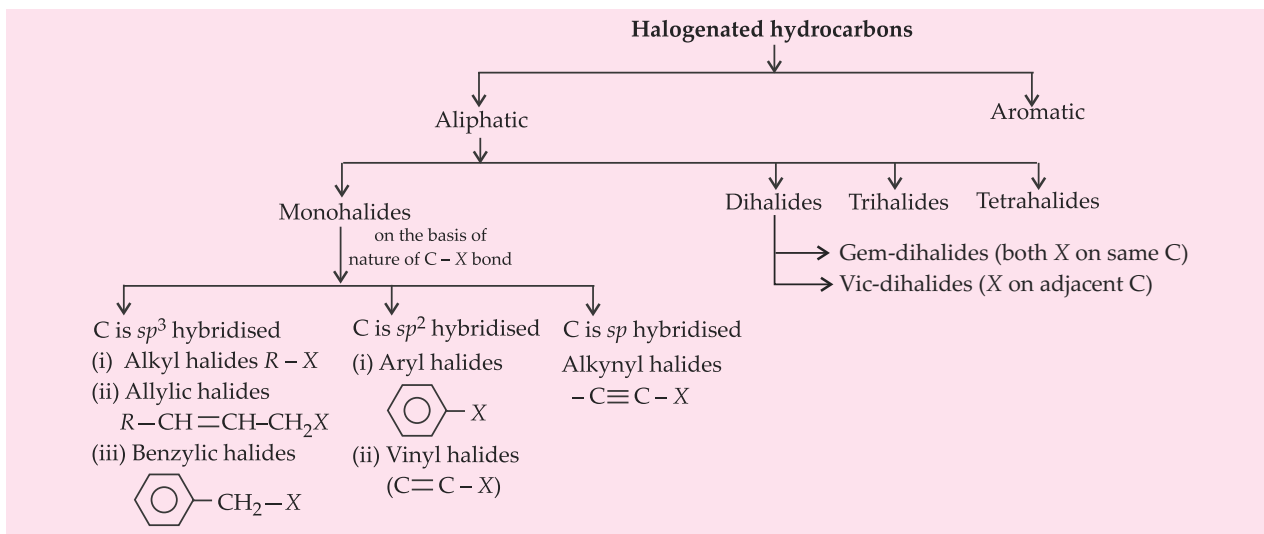
ORGANIC COMPOUNDS CONTAINING HALOGENS

- Preparations, Properties and Reactions
- Nature of C - X bond
- Uses and Environmental Effects of Chloroform, Iodoform, Freons and DDT

TIPS TO REMEMBER

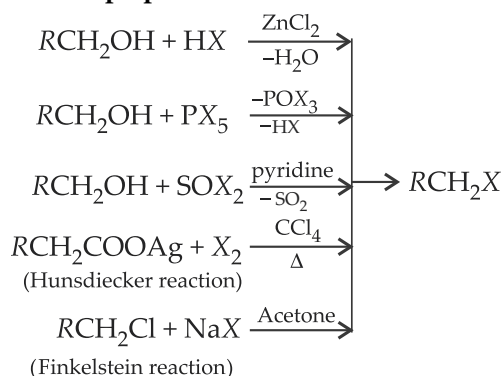
- Halogen derivatives are derived from hydrocarbons by the replacement of one or more hydrogen atoms with halogens.

Classification

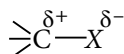


Aliphatic halogen derivatives

Methods of preparation :



- **Nature of C—X bond :** C—X bond is highly polarised because X is more electronegative than C. Thus, haloalkanes are highly reactive towards nucleophilic substitution reactions.



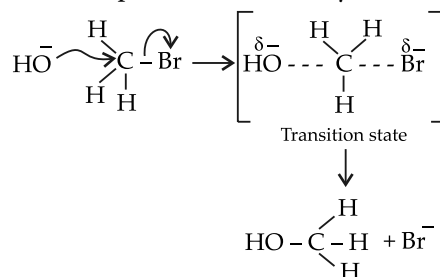
- **Order of reactivity :**
C—F < C—Cl < C—Br < C—I
- **Order of bond length :**
C—F < C—Cl < C—Br < C—I
- **Order of bond enthalpy :**
C—F > C—Cl > C—Br > C—I
- **Order of dipole moment :**
C—Cl > C—F > C—Br > C—I
- Haloarenes are less reactive towards nucleophilic substitution reactions than haloalkanes. This low reactivity can be attributed to the following factors:
 - The C—X bond in halobenzene has a partial double bond character due to involvement

of halogen electrons in resonance with benzene ring.

- The C—X bond in aryl halides is less polar as compared to that in alkyl halides as sp^2 hybridised carbon is more electronegative than sp^3 hybridised carbon.

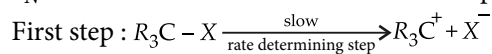
Mechanism of substitution reaction :

- **S_N2 reaction :** The mechanism is a one step concerted mechanism in which attack of nucleophile and the displacement of the halide ions take place simultaneously.

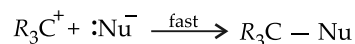


- **Order of reactivity towards S_N2 reaction :**
CH₃—X > CH₃CH₂—X > (CH₃)₂CH—X > (CH₃)₃C—X
- Rate of S_N2 reaction depends upon the concentration of halide and nucleophile both so it is called *bimolecular nucleophilic substitution*. S_N2 reaction proceeds through inversion of configuration.

- **S_N1 reaction :** Mechanism involves two steps :

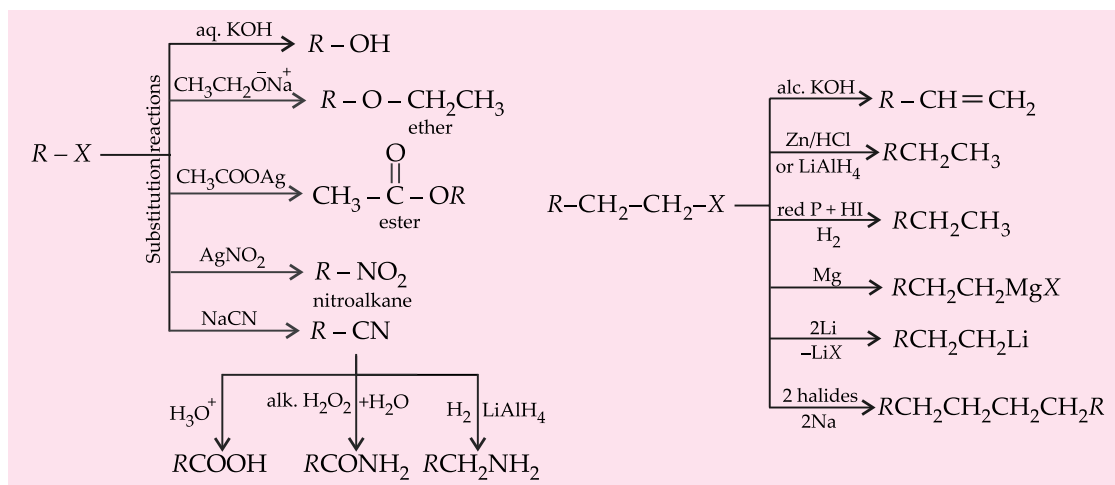


Second step :

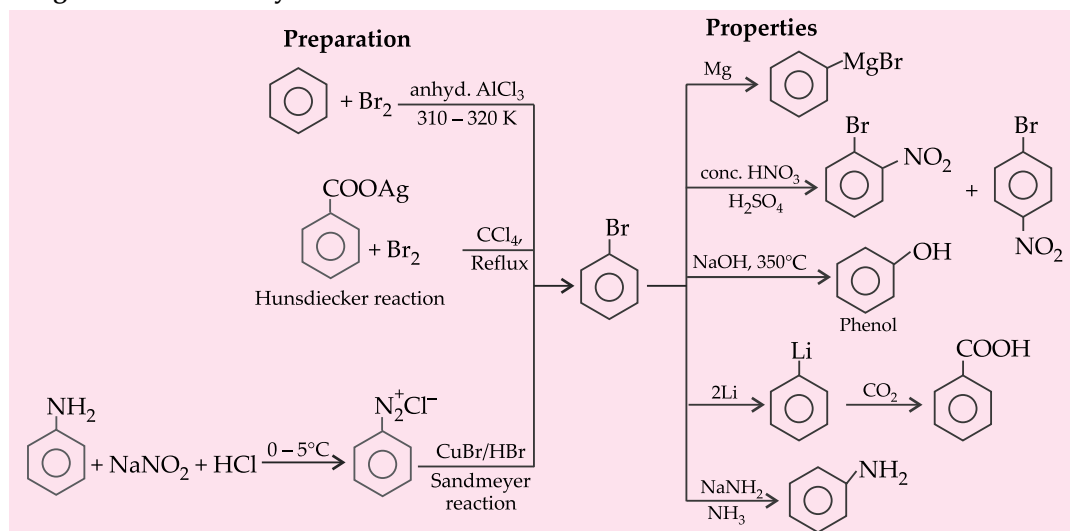


So, rate depends only upon the concentration of halide because it is only participating in slow or rate determining step.

— **Reactivity order:** $(\text{CH}_3)_3\text{C}-\text{X} > (\text{CH}_3)_2\text{CHX} > \text{CH}_3\text{CH}_2\text{X} > \text{CH}_3-\text{X}$



Aromatic halogen derivatives (Aryl halides)



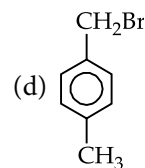
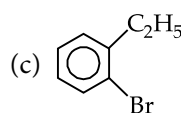
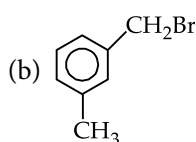
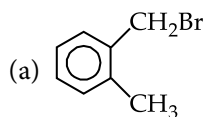
KEY POINT

- Direct iodination is not possible as it is a reversible reaction hence, it is carried out in presence of an oxidising agent like HIO_3 or HNO_3 .
- The presence of electron withdrawing groups like $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$ etc., in *ortho* and *para* positions makes the halogen atom easily replaceable while the presence of electron releasing groups like $-\text{NH}_2$, $-\text{OH}$, $-\text{OR}$ etc. decreases the reactivity.

SELF CHECK

- The synthesis of alkyl fluorides is best accomplished by
 - Finkelstein reaction
 - Swart's reaction
 - free radical fluorination
 - Sandmeyer's reaction.
 (JEE Main 2015)
- The major organic compound formed by the reaction of 1,1,1-trichloroethane with silver powder is
 - 2-butene
 - acetylene
 - ethene
 - 2-butyne
 (JEE Main 2014)
- In $\text{S}_{\text{N}}2$ reactions, the correct order of reactivity for the following compounds :
 CH_3Cl , $\text{CH}_3\text{CH}_2\text{Cl}$, $(\text{CH}_3)_2\text{CHCl}$ and $(\text{CH}_3)_3\text{CCl}$ is
 - $(\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_3\text{CCl}$
 - $\text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_3\text{CCl}$
 - $\text{CH}_3\text{Cl} > \text{CH}_3\text{CH}_2\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$
 - $\text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$
 (JEE Main 2014)

18. Compound (A), C_8H_9Br , gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A).



(JEE Main 2013)

Uses and Environmental Effects of Some Important Compounds

Compounds	Uses	Effects
Chloroform ($CHCl_3$)	<ul style="list-style-type: none"> Its major use is in the production of Freon refrigerant, R-22. It is used as a solvent for resins, rubbers, oils and fats, alkaloids, iodine and many other substances. In the past, it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage. It is used in preparation of chloretone (drug) and chloropicrin (insecticide). It is used to preserve anatomical species. 	<ul style="list-style-type: none"> It is oxidised to poisonous gas, carbonyl chloride, known as <i>phosgene</i>. $2CHCl_3 + O_2 \xrightarrow{\text{Light}} 2COCl_2 + 2HCl$ Phosgene gas causes liver and kidney damage. Inhaling chloroform vapours depresses the CNS, causes dizziness, fatigue and headache.
Iodoform (CHI_3)	<ul style="list-style-type: none"> It is used as an antiseptic in dressing of wounds due to liberation of iodine. It is used as methylating agent in organic synthesis. 	<ul style="list-style-type: none"> It has strong smell.
Freons	<ul style="list-style-type: none"> They are used as refrigerants, blowing agents, propellants in medical applications and degreasing solvent. 	<ul style="list-style-type: none"> Freons cause disruption of ozone layer by initiating radical chain reactions in stratosphere. This anthropogenic compound is a green-house gas and its effect is more than CO_2.
DDT	<ul style="list-style-type: none"> In 1940, it was used as a pesticide. 	<ul style="list-style-type: none"> It is a persistent organic pollutant, strongly absorbed by soil. It is lipophilic so has a high potential to bioaccumulate. It may be directly genotoxic but may also induce enzymes to produce other genotoxic intermediates and DNA adducts.

KEY POINT

- Iodoform has antiseptic properties because on coming in contact with organic matter of skin it decomposes to give free iodine which is an antiseptic.
- Before using the sample of chloroform as an anaesthetic it is tested by treating with aqueous solution of $AgNO_3$. A pure sample does not give precipitate with $AgNO_3$.

ANSWER KEYS (SELF CHECK)

1. (c) 2. (c) 3. (a) 4. (b) 5. (c)
 6. (c) 7. (c) 8. (a) 9. (b) 10. (a)
 11. (a) 12. (b) 13. (d) 14. (b) 15. (b)
 16. (d) 17. (c) 18. (a)



Exam Café

QUESTIONS FOR PRACTICE

- There are several criteria of purity of organic compounds. Which is considered to be the best?
 - Melting point
 - Mixed melting point
 - Colour
 - Microscopic examination
- The most satisfactory method of separating sugars from each other is
 - fractional crystallisation
 - sublimation
 - chromatography
 - distillation.
- Azeotropes are
 - liquid mixtures, which distil unchanged in composition
 - liquids mixed in equal proportions
 - solids which form solutions of definite composition
 - gaseous mixtures, which cannot be separated.
- Liquids which decompose below their normal boiling points can be distilled at lower temperature by
 - increasing the pressure
 - decreasing the pressure
 - heating in water bath
 - heating in sand bath.
- In a Lassaigne's test for sulphur in the organic compound with sodium nitroprusside solution the violet colour formed is due to
 - $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$
 - $\text{Na}_3[\text{Fe}(\text{CN})_5\text{S}]$
 - $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NOS}]$
 - $\text{Na}_3[\text{Fe}(\text{CN})_6]$
- In Lassaigne's test sodium metal is used because
 - it is very reactive
 - its melting point is low
 - its compounds are soluble in water
 - all of the above.
- In the estimation of nitrogen by Dumas method 1.18 g of an organic compound gave 224 mL of N_2 at STP. The percentage of nitrogen in the compound is about
 - 20.0
 - 11.8
 - 47.5
 - 23.7
- Which of the following statements is incorrect?
 - Using Lassaigne's test, nitrogen and sulphur present in an organic compound can be tested.
 - Using Beilstein's test, the presence of halogens in a compound can be tested.
 - In Lassaigne's filtrate, the nitrogen in an organic compound is converted to NaCN .
 - In the estimation of carbon, an organic compound is heated with CaO in a combustion tube.
- The IUPAC name of

$$\text{CH}_3\text{CH}=\text{CHCH}_2\underset{\text{NH}_2}{\text{CH}}\text{CH}_2\text{COOH}$$
 is
 - 5-aminohept-2-enoic acid
 - β -amino- δ -heptanoic acid
 - 5-aminohept-2-enecarboxylic acid
 - 3-aminohept-5-enoic acid.
- Among the following carbocations,
 - $\text{Ph}_2\text{C}^+\text{CH}_2\text{Me}$
 - $\text{PhCH}_2\text{CH}_2\text{CH}^+\text{Ph}$
 - $\text{Ph}_2\text{CHCH}^+\text{Me}$
 - $\text{Ph}_2\text{C}(\text{Me})\text{CH}_2^+$
 the order of stability is
 - $\text{IV} > \text{II} > \text{I} > \text{III}$
 - $\text{I} > \text{II} > \text{III} > \text{IV}$
 - $\text{II} > \text{I} > \text{IV} > \text{III}$
 - $\text{I} > \text{IV} > \text{III} > \text{II}$
- The enol form of acetone after treatment with D_2O gives
 - $\text{CH}_3-\overset{\text{OD}}{\underset{|}{\text{C}}}=\text{CH}_2$
 - $\text{CH}_3-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CD}_3$
 - $\text{CH}_2=\overset{\text{OH}}{\underset{|}{\text{C}}}-\text{CH}_2\text{D}$
 - $\text{CD}_2=\overset{\text{OD}}{\underset{|}{\text{C}}}-\text{CD}_3$
- Allylic bromination of an olefin is
 - nucleophilic substitution
 - electrophilic substitution
 - free radical substitution
 - electrophilic addition.
- The strongest base among the following is
 - NH_4^+
 - $:\text{NH}_3$
 - NH_2^-
 - OH^-

14. What is the relationship between keto and enol tautomers?
 (a) Resonance forms
 (b) Constitutional isomers
 (c) Stereoisomers
 (d) Different conformations of the same compound
15. In the following reaction, the product 'R' is

$$\text{CaC}_2 \xrightarrow{\text{H}_2\text{O}} \text{P} \xrightarrow[\text{tube}]{\text{hot iron}} \text{Q} \xrightarrow[\text{anhyd. AlCl}_3]{\text{CH}_3\text{Cl}} \text{R}$$

 (a) benzene (b) ethylbenzene
 (c) toluene (d) *n*-propylbenzene.
16. In the compound $\begin{array}{c} \text{}^1\text{COOH} \\ | \\ \text{H} - \text{}^2\text{C} - \text{OH} \\ | \\ \text{HO} - \text{}^3\text{C} - \text{H} \\ | \\ \text{}^4\text{COOH} \end{array}$ configurations are
 (a) *R, R* (b) *R, S*
 (c) *S, R* (d) *S, S*
17. In presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov's addition to alkenes because
 (a) both are highly ionic
 (b) one is oxidising and the other is reducing
 (c) one of the steps is endothermic in both cases
 (d) all steps are exothermic in both cases.
18. An alkane C_7H_{16} is produced by the reaction of lithium di-3-pentylcuprate with ethyl bromide. The structural formula of product is
 (a) 3-methylhexane
 (b) 2-ethylpentane
 (c) 3-ethylpentane
 (d) *n*-heptane.
19. Using AlCl_3 and HCl as catalyst, which one of the following reactions produces ethylbenzene?
 (a) $\text{H}_3\text{C} - \text{CH}_2\text{OH} + \text{C}_6\text{H}_6$
 (b) $\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{C}_6\text{H}_6$
 (c) $\text{H}_2\text{C} = \text{CH}_2 + \text{C}_6\text{H}_6$
 (d) $\text{H}_3\text{C} - \text{CH}_3 + \text{C}_6\text{H}_6$
20. The compound X (C_5H_8) reacts with ammoniacal AgNO_3 to give a white precipitate, and on oxidation with hot alkaline KMnO_4 gives the acid, $(\text{CH}_3)_2\text{CHCOOH}$. Therefore, X is
 (a) $\text{CH}_2 = \text{CHCH} = \text{CHCH}_3$
 (b) $\text{CH}_3(\text{CH}_2)_2\text{C} \equiv \text{CH}$
 (c) $(\text{CH}_3)_2\text{CH} - \text{C} \equiv \text{CH}$
 (d) $(\text{CH}_3)_2\text{C} = \text{C} = \text{CH}_2$
21. A hydrocarbon of formula C_6H_{10} absorbs only one molecule of H_2 upon catalytic hydrogenation. Upon ozonolysis the hydrocarbon yields

$$\begin{array}{c} \text{H} \qquad \qquad \qquad \text{H} \\ | \qquad \qquad \qquad | \\ \text{O}=\text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{C}=\text{O} \end{array}$$

 The hydrocarbon is
 (a) cyclohexane (b) benzene
 (c) cyclohexene (d) cyclobutane.
22. Ethoxyethane and methoxypropane are
 (a) geometrical isomers
 (b) optical isomers
 (c) functional group isomers
 (d) metamers.
23. When *neo*-pentyl bromide is subjected to Wurtz reaction, the product formed is
 (a) 2,2,4,4-tetramethylhexane
 (b) 2,2,4,4-tetramethylpentane
 (c) 2,2,5,5-tetramethylhexane
 (d) 2,2,3,3-tetramethylhexane.
24. The product formed during the reaction is

$$\text{CH} \equiv \text{CH} + \text{NaOCl} \xrightarrow{0^\circ\text{C}}$$

 (a) 1,2-dichloroethane (b) 1,2-dichloroethenal
 (c) 1,2-dichloroethene (d) 1,2-dichloroethyne.
25. 1-Chlorobutane on reaction with alcoholic potash gives
 (a) 1-butene (b) 1-butanol
 (c) 2-butene (d) 2-butanol.
26. Iodoform when treated with silver powder forms
 (a) methane (b) ethane
 (c) ethene (d) ethyne.
27. An alkyl chloride (A) produces a single alkene on reaction with sodium ethoxide and ethanol. The alkene further undergoes hydrogenation to yield 2-methylbutane. The alkyl chloride (A) is
 (a) $\text{ClCH}_2\text{C}(\text{CH}_3)_3$
 (b) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
 (c) $\text{ClCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
 (d) $\text{CH}_3\text{C}(\text{Cl})(\text{CH}_3)\text{CH}_2\text{CH}_3$
28. Which of the following is the best scientific method to test presence of water in a liquid?
 (a) Smell
 (b) Taste
 (c) Use of litmus paper
 (d) Use of anhydrous copper sulphate

29. A sample of chloroform before being used as an anaesthetic is tested by
- AgNO₃ solution
 - AgNO₃ solution after boiling with alc. KOH
 - Fehling's solution
 - ammoniacal Cu₂Cl₂.
30. Toluene on reaction with *N*-bromosuccinimide gives
- p*-bromomethylbenzene
 - o*-bromomethylbenzene
 - phenylbromomethane
 - m*-bromomethylbenzene.

SOLUTIONS

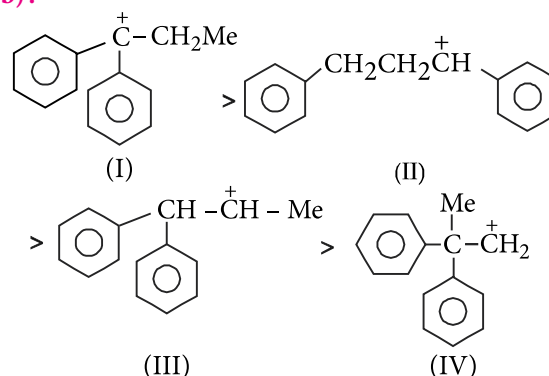
1. (b): Mixed melting point is considered to be the best criteria for purity of a substance. The purified sample is mixed with a small quantity of pure compound and melting point of mixture is determined. If melting point of mixture is same as that of the pure compound, the sample compound is pure, otherwise it requires further purification.
2. (c): Best method to separate many components from a mixture is chromatography.
3. (a): Azeotropes are constant boiling liquid mixtures which distil without any change in composition.
4. (b): By decreasing the pressure, their boiling points can be lowered.
5. (a):
- $$\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$$
- (From Lassaigne's extract) Sodium nitroprusside Sodium thionitroprusside (Violet colour)
6. (d): Sodium metal fulfills all the requirements.
7. (d): Percentage of nitrogen

$$= \frac{28}{22400} \times \frac{\text{Volume of N}_2 \text{ at STP}}{\text{Weight of organic compound}} \times 100$$

$$= \frac{28}{22400} \times \frac{224}{1.18} \times 100 = 23.73\%$$

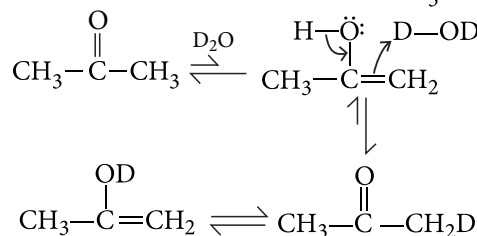
8. (d): In the estimation of carbon, organic compound is heated with excess of oxygen and CuO.
9. (d): $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \underset{\text{NH}_2}{\text{CH}} - \text{CH}_2 - \text{COOH}$
- 3-Aminohept-5-enoic acid

10. (b):



Stability of carbocations depends upon the number of resonating structures and the extent of +I, and -I effects.

11. (a): The enol form of acetone is $\text{CH}_3 - \text{C}(\text{OH}) = \text{CH}_2$.



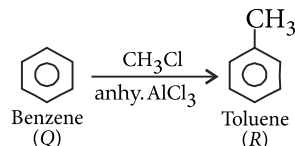
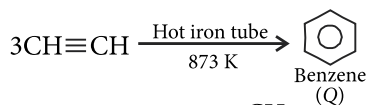
12. (c): It is a free radical substitution reaction.

13. (c): Conjugate acid of NH_2^- i.e., NH_3 is the weakest acid among the given compounds, thus, NH_2^- is the strongest base.

14. (b): Keto-enol tautomers have same molecular formula but different functional groups and exist in dynamic equilibrium with each other hence, they are constitutional isomers.

15. (c): $\text{CaC}_2 + 2\text{H}_2\text{O} \longrightarrow \text{HC}\equiv\text{CH} + \text{Ca}(\text{OH})_2$

Calcium carbide Acetylene (P)



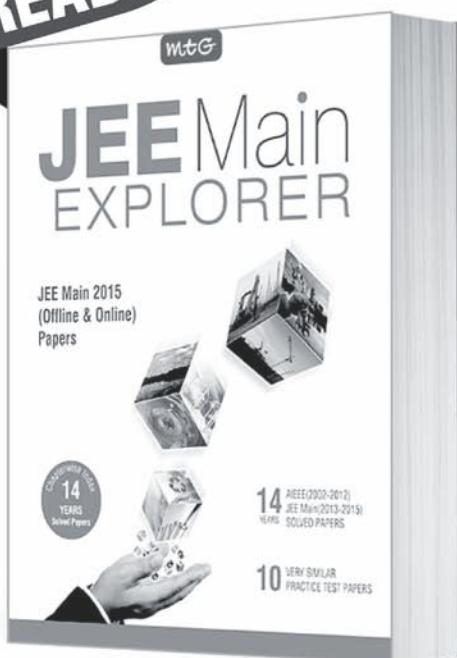
∴ Product 'R' is toluene.

16. (a):

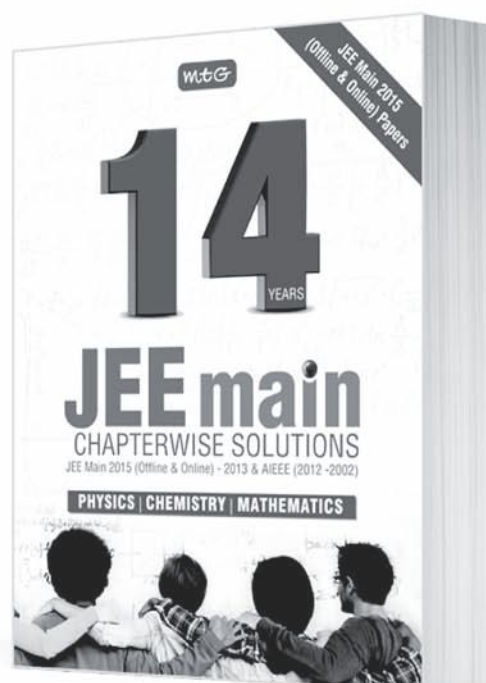
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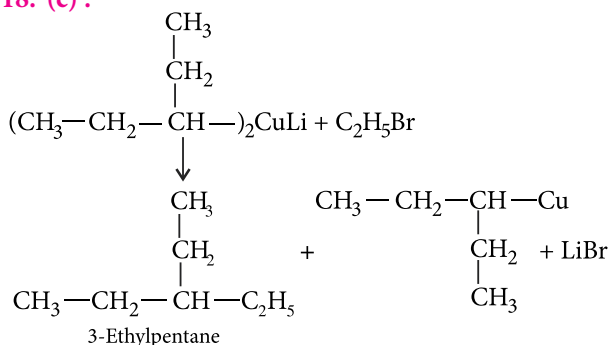
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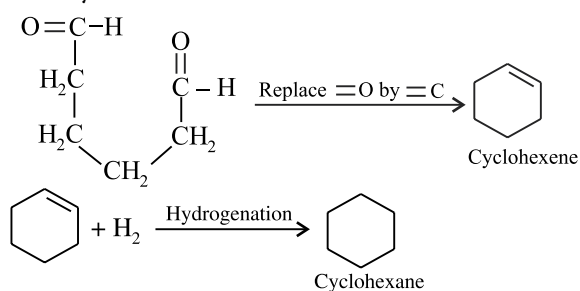
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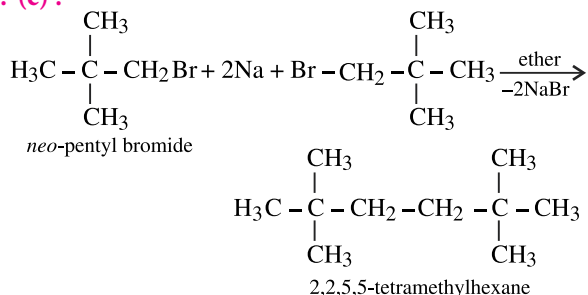
18. (c) :


$$\text{CH}_2=\text{CH}_2 \xrightarrow{\text{H}^+, \text{AlCl}_3} \text{CH}_3-\overset{+}{\text{CH}}_2 \xrightarrow{\text{C}_6\text{H}_6} \text{C}_6\text{H}_5\text{C}_2\text{H}_5$$

21. (c) : The parent alkene can be obtained by replacing $=O$ by $=C$.



23. (c) :


$$\text{HC}\equiv\text{CH} + 2\text{NaOCl} \xrightarrow{0^\circ\text{C}} \text{Cl}-\text{C}\equiv\text{C}-\text{Cl} + 2\text{NaOH}$$
$$\text{ClCH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3 \xrightarrow{\text{alc.KOH}} \text{CH}_2=\text{CH—CH}_2\text{—CH}_3$$

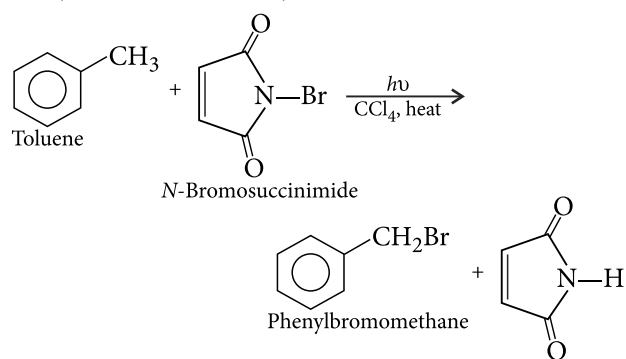
1-Chlorobutane But-1-ene

$$\text{CH}_3\text{I}_3 + 6\text{Ag} + \text{I}_3\text{CH} \xrightarrow{\Delta} \text{HC} \equiv \text{CH} + 6\text{AgI}$$

Ethyne

$$\begin{array}{ccc} \text{CH}_3 & & \text{CH}_3 \\ | & & | \\ \text{ClCH}_2-\text{CH}-\text{CH}_2-\text{CH}_3 & \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{NaOEt}} & \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}_3 \\ A & & \downarrow \text{H}_2 \\ & & \text{CH}_3 \\ & & | \\ & & \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\ & & \text{2-Methylbutane} \end{array}$$
$$\underset{\text{White}}{\text{CuSO}_4} + 5\text{H}_2\text{O} \longrightarrow \underset{\text{Blue}}{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}$$

30. (c) : Allylic bromination takes place by NBS (free-radical reaction).



ACE

YOUR WAY CBSE XII



Series 7

CHAPTERWISE PRACTICE PAPER :

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS | AMINES

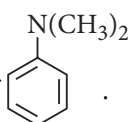
Time Allowed : 3 hours

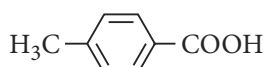
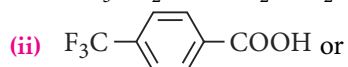
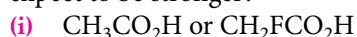
Maximum Marks : 70

GENERAL INSTRUCTIONS

- All questions are compulsory.
- Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- Q. no. 23 is a value based question and carries 4 marks.
- Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- Use log tables if necessary, use of calculators is not allowed.

- Which type of aldehydes undergo Cannizzaro reaction?
- How is acetone obtained from 2-bromopropane?
- What is esterification?

- Write down the IUPAC name of .
- What is the order of basicity of 1°, 2° and 3° ethyl substituted amines in aqueous solution?
- An organic compound 'A' with molecular formula $C_5H_8O_2$ is reduced to *n*-pentane on treatment with Zn-Hg/HCl. 'A' forms a dioxime with hydroxylamine and gives a positive iodoform and Tollens' test. Identify the compound 'A' and deduce its structure.
- Which acid of each pair shown here would you expect to be stronger?



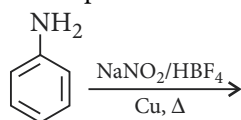
OR

- Carboxylic acids are higher boiling liquids as compared to corresponding aldehydes, ketones or alcohols. Explain.
- What happens when primary alcohols are oxidised by potassium permanganate?
- When propanone is subjected to Wolff Kishner reduction, what product will be obtained? Give chemical equation.
- How will you convert acetaldehyde to acetone?
- Mention two important uses of sulphanilic acid.
- Which amino compounds are used as surfactants?
- What is the order of boiling points of isomeric amines?
- Write the reactions with conditions for the following conversions :
 - Methanal to propan-1-ol
 - Benzaldehyde to benzyl alcohol
 - Benzaldehyde to benzophenone

12. Explain the following observations :
- In aqueous solution the K_b order is $\text{Me}_2\text{NH} > \text{MeNH}_2 > \text{Me}_3\text{N}$
 - The diazonium ion acts as an electrophile.
 - Tertiary amines do not undergo acylation reaction.
13. (i) How will you convert :
- Propanone to propan-2-ol.
 - Propanone to 2-methyl-2-propanol.
- (Write the reaction and state the reaction conditions in each case.)
- (ii) Write a distinction test for acetaldehyde and acetone.
14. (i) Carboxylic acids are more acidic than phenols. Why?
- (ii) The carboxylic carbon is less electrophilic than carbonyl carbon. Explain.
15. (i) How will you convert :
- Benzene into aniline
 - 3-Methylaniline into 3-nitrotoluene
- (ii) Give one chemical test to distinguish between aniline and *N*-methylaniline.

OR

- (a) Account for the following :
Like ammonia, amines are good nucleophiles.
(b) Aryl amines are weaker bases than alkyl amines.
- Predict the product of the following reaction :



16. Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents :
- PhMgBr and then H_3O^+
 - Semicarbazide and weak acid
 - Excess of ethanol and dry hydrogen chloride gas
17. (i) Describe the following giving a chemical equation for each :
- Cannizzaro reaction
 - Trans-esterification
- (ii) Account for the following :
Electrophilic substitution in benzoic acid takes place at *meta*-position.

18. Explain the following :

- tert*-Butylbenzene does not give benzoic acid on oxidation with acidic KMnO_4 . Give reasons.
 - The carbonyl oxygen atom of a carboxylic acid is more basic than hydroxyl oxygen.
19. (i) An organic compound 'A' having molecular formula $\text{C}_2\text{H}_7\text{N}$ on treatment with HNO_2 gave an oily yellow substance. Identify 'A'.
- (ii) How are 1°, 2° and 3°-amines distinguished?
20. (i) Identify the substances 'A' and 'B'.
- $$\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{A} \xrightarrow{\text{Heat}} \text{B}$$
- (ii) Why is benzenediazonium chloride not stored and is used immediately after its preparation?
- (iii) Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?
21. (i) Explain the mechanism of the following reaction :
Addition of Grignard reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis.
- (ii) Write the structure of 4-chloropentan-2-one.
- (iii) Name the products formed on oxidation of 2, 5-dimethylhexan-3-one.

22. (i) Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.
- Ethanal, Propanal, Propanone, Butanone.
 - Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.
- (ii) Give plausible explanation for the following :
During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.
23. During the chemistry practical in laboratory, Piyush removed labels from the bottles of acetaldehyde and acetone to irritate lab assistants. His classmate, Abhishek who noticed his act told him that he should not play with the chemicals like this as it could be dangerous for us.
- What values are shown by Abhishek?
 - How can these chemicals be distinguished for correct labelling?
 - Name two methods which are commonly used to convert $>\text{C}=\text{O}$ group present in acetaldehyde and acetone into a $>\text{CH}_2$ group.
 - Write two uses of acetone.

24. Compound 'A' ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yields two compounds 'B' and 'C'. The compound 'B' on oxidation gives 'D' which on treatment with aqueous alkali and subsequent heating furnishes 'E'. The latter on catalytic hydrogenation gives 'C'. The compound 'D' on further oxidation gives CH_3COOH . Deduce the structures of A, B, C, D and E.

OR

- (i) What happens when
 (a) malonic acid is heated with urea in presence of $POCl_3$
 (b) ethanal reacts with air in presence of cobalt acetate?
- (ii) Illustrate the following name reactions :
 (a) Cross aldol condensation
 (b) Hell-Volhard-Zelinsky reaction
25. (i) How can you prepare monobromoaniline from aniline?
 (ii) Explain the following :
 (a) Coupling reaction of a diazonium salt.
 (b) Aqueous ethylamine turns red litmus blue.
 (c) Methylamine in water reacts with ferric chloride to precipitate ferric hydroxide.

OR

- (i) Although amino group is *o*, *p*-directing in aromatic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
 (ii) How will you prepare the following compounds from benzenediazonium chloride :
 (a) Benzene (b) A yellow dye
 (c) An orange dye?
26. (i) Addition of ammonia derivatives to carbonyl compound takes place in weakly acidic medium ($pH = 3.5$) only. Why?
 (ii) Carbonyl carbon is an electrophilic whereas carbonyl oxygen is a nucleophilic centre. Why?
 (iii) How are formalin and trioxane related to methanal?

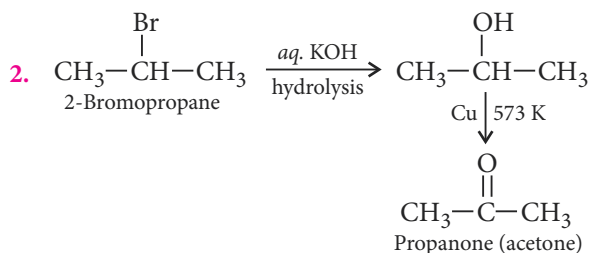
OR

An aromatic compound 'A' (C_8H_8O) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give

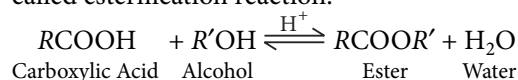
Tollens' or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid 'C' ($C_7H_6O_2$), which is also formed along with the yellow compound in the above reaction. Identify A, B and C and write all the reactions involved.

SOLUTIONS

1. Those aldehydes which do not have an α -hydrogen, undergo Cannizzaro reaction. *e.g.*, $HCHO$, C_6H_5CHO .



3. Carboxylic acids on reaction with alcohols or phenols in the presence of a mineral acid such as conc. H_2SO_4 or HCl gas form ester. This reaction is called esterification reaction.



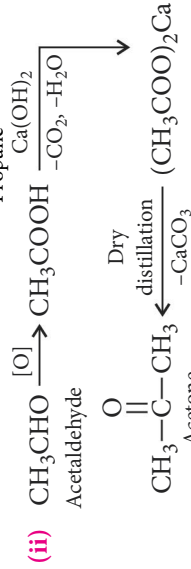
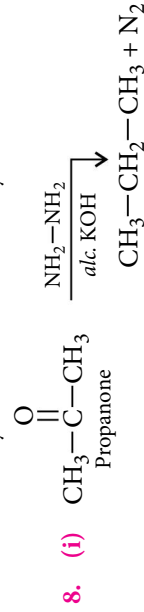
4. *N,N*-Dimethylbenzenamine
5. Order of basicity of ethyl substituted amines is : $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$ due to steric hindrance to H-bonding, +I effect predominates.
6. (i) The organic compound 'A' ($C_5H_8O_2$) is reduced to *n*-pentane on treatment with $Zn-Hg/HCl$ and gives positive iodoform test. Hence, it may be an aldehyde or ketone containing chain of 5-carbon atoms.
 (ii) Since it gives positive Tollens' test, it must be an aldehyde.
 (iii) It forms dioxime with hydroxylamine therefore, it contains two aldehydic groups.
 Thus, the compound 'A' is

$$OHC-CH_2-CH_2-CH_2-CHO$$
 Pentane-1, 5-dial
7. (i) H_2FCOOH will be stronger of the two. The presence of electronegative F-atom at the α -C causes electron withdrawal from the $-COOH$ and facilitates the release of H^+ .
 (ii) $F_3C-\text{C}_6\text{H}_4-\text{COOH}$ is more acidic due to the presence of electron withdrawing $-CF_3$ group in it.

OR

(i) Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses due to more extensive association of carboxylic acid molecules by intermolecular hydrogen bonding.

(ii) Primary alcohols on oxidation with potassium permanganate give carboxylic acids.

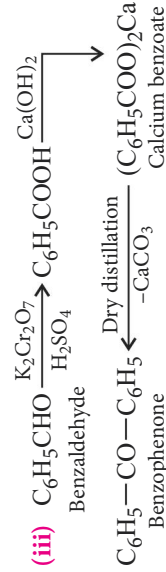
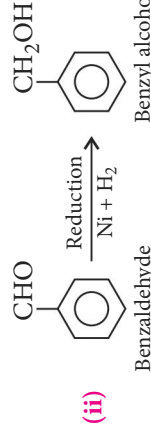
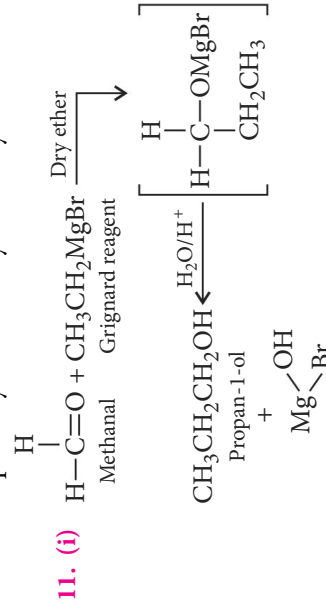


9. (i) Sulphanilic acid is used in the manufacture of dyes.

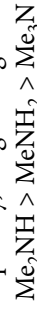
(ii) It is used in the preparation of sulpha drugs such as sulphathiazole, sulphapyridine, etc.

10. (i) Quaternary ammonium salts are used as surfactants.

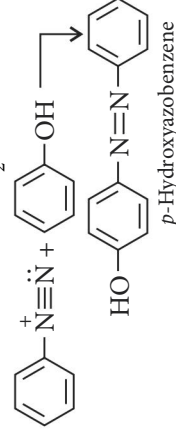
(ii) The order of boiling points of isomeric amines is primary > secondary > tertiary.



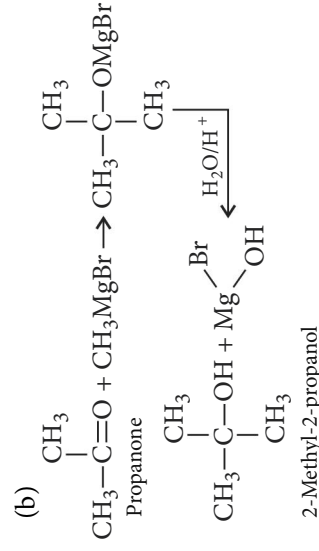
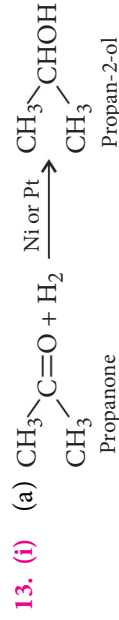
12. (i) In alkyl amines, a combination of +I effect of alkyl groups, steric factors and H-bonding factors determine the stability of ammonium cations in aqueous solution. All these factors are favourable for 2° amines and for smaller -CH₃ group, stability due to hydrogen bonding predominates over the stability due to +I effect. Consequently, we get the given K_b order :



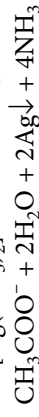
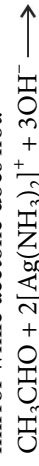
(ii) The diazonium ion is electrophile because there is positive charge on terminal nitrogen. It can react with nucleophilic aromatic compound (Ar - H) activated by electron donating groups such as -OH and -NH₂.



(iii) Tertiary amines do not undergo acylation reaction because they do not contain any H-atom on the nitrogen atom.



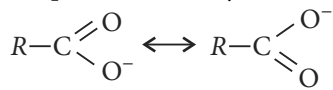
(ii) Acetaldehyde reduces Tollens' reagent to silver mirror while acetone does not.



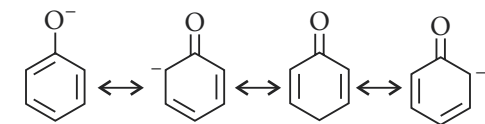
CH₃COCH₃ + Tollens' reagent → No reaction

14. (i) The higher acidity of carboxylic acid as compared to phenol is due to the stabilisation of carboxylate ion by two resonating structures in which -ve charge is at the more electronegative oxygen. But in resonating structures of phenoxide ion the -ve charge is at less electronegative carbon atom. So,

resonance stabilisation in phenoxide ion is less as compared to carboxylate ion.

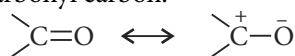


Carboxylate ion

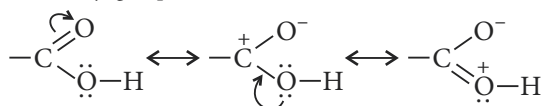


Phenoxide ion

- (ii) Due to resonating structures of carboxylate ion, carboxylic carbon is less electrophilic than carbonyl carbon.

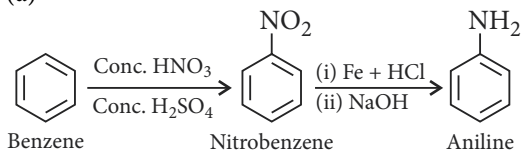


Carbonyl group

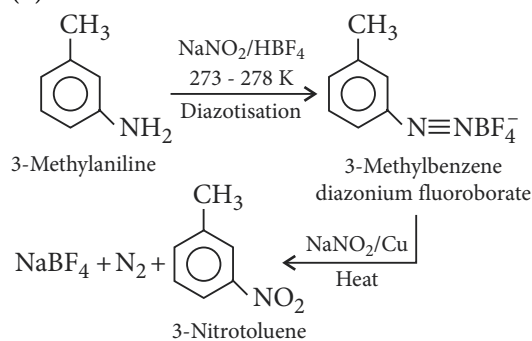


Carboxyl group

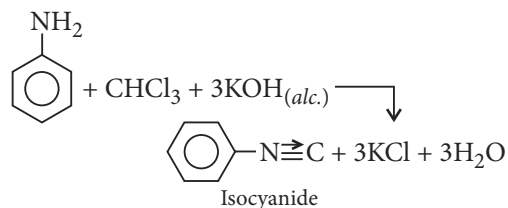
15. (i) (a)



- (b)

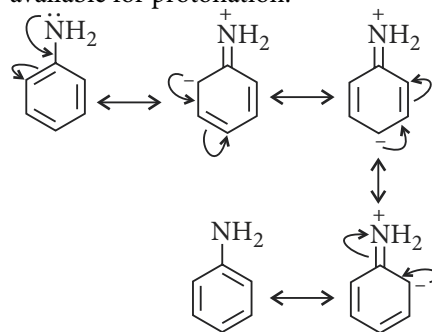


- (ii) Aniline and *N*-methylaniline can be distinguished by carbylamine test. Aniline, the primary amine on heating with chloroform in presence of alcoholic KOH forms isocyanide having unpleasant smell.

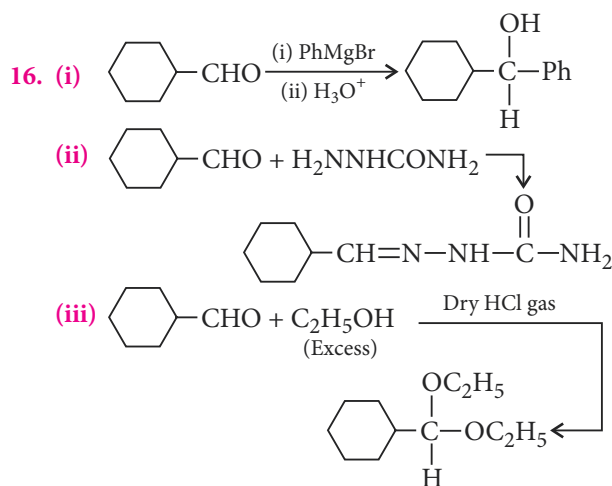
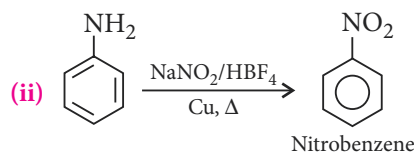


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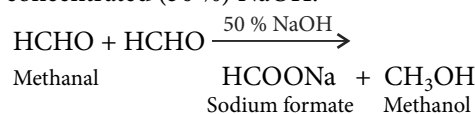
- (i) (a) Amines like ammonia are good nucleophiles. This is because alkyl group in an amine shows electron releasing effect. This increases the electron density on 'N' of amino group and hence, makes the amines very good nucleophiles.
(b) Due to resonance in aniline, the lone pair of electrons on nitrogen gets delocalised over the benzene ring and becomes less available for protonation.



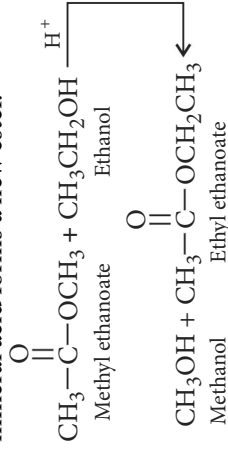
In alkyl amine, alkyl group releases electrons and increases electron density on nitrogen, making it stronger base.



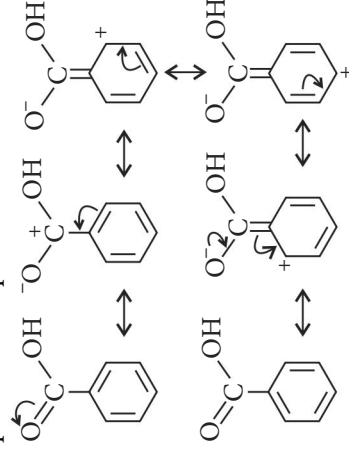
17. (i) (a) Cannizzaro reaction : Aldehydes which do not contain an α -H atom undergo disproportionation when heated with concentrated (50 %) NaOH.



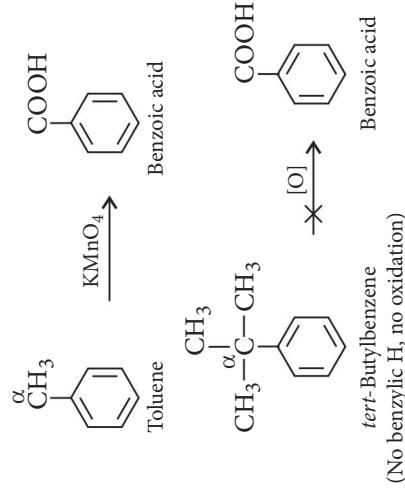
- (b) Trans-esterification : An ester on reaction with excess of alcohol in the presence of mineral acid forms a new ester.



- (ii) There is high electron density at *meta*-position due to resonance in benzoic acid. Therefore, electrophilic substitution in benzoic acid takes place at *meta*-position.

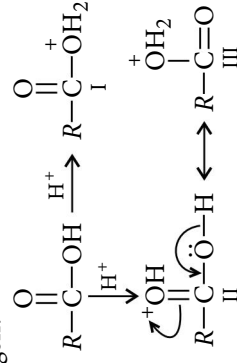


18. (i) Due to absence of benzylic hydrogens, *tert*-butylbenzene does not undergo oxidation to give benzoic acid while other alkylbenzenes such as toluene, ethylbenzene, *n*-propylbenzene and isopropylbenzene which contain one or more benzylic hydrogens undergo oxidation to form benzoic acid.

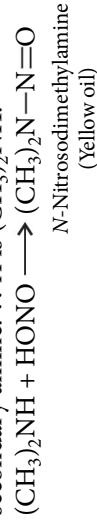


- (ii) Protonation at the hydroxyl oxygen of a carboxylic acid gives structure (I) but protonation at the carbonyl oxygen gives structure (II) which can be regarded as a resonance hybrid of two structures (II and III). Thus, structure (II) is more stable than

structure (I) and hence, carbonyl oxygen atom of a carboxylic acid is more basic than hydroxyl oxygen.

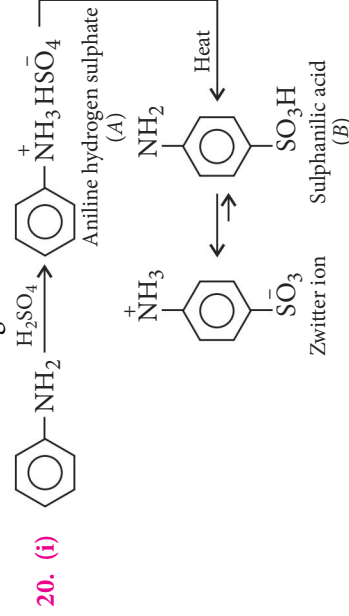


19. (i) The compound 'A' gives a yellow oily substance on treatment with HNO_2 . So, it must be a secondary amine. \therefore A is $(\text{CH}_3)_2\text{NH}$.



- (ii) 1°, 2° and 3° amines are distinguished by Hinsberg's test. 1° amines react with benzenesulphonyl chloride to give *N*-alkylbenzenesulphonamide which is soluble in alkali. 2° amines give *N,N*-dialkylbenzenesulphonamide which is insoluble in alkali and remain unaffected on addition of acid.

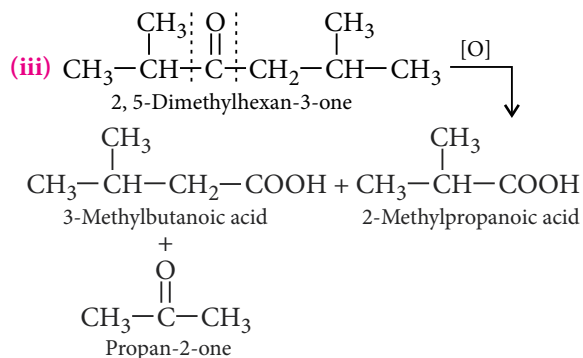
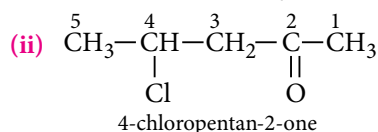
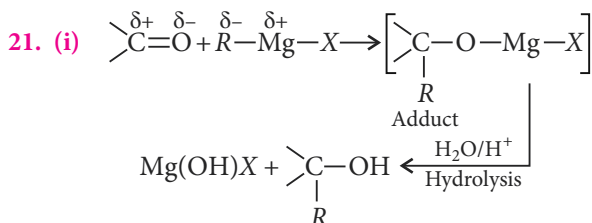
3° amines do not react at all and remain insoluble in alkaline solution but dissolves on acidification to give a clear solution.



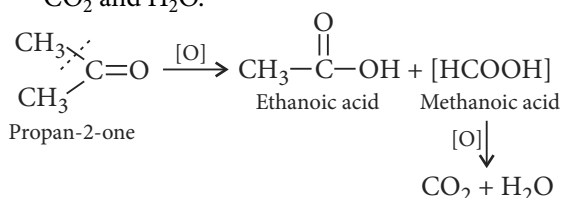
- (ii) Benzenediazonium chloride is readily soluble in water and is stable in cold water for short time only. It decomposes easily in dry state hence, cannot be stored and is used immediately after preparation.

- (iii) The key step in the Gabriel phthalimide synthesis is a $\text{S}_{\text{N}}2$ reaction in which the nucleophile, phthalimide anion displaces the halide ion from alkyl halide to form *N*-alkylphthalimide. This upon subsequent acid or alkaline hydrolysis gives the corresponding aliphatic primary amine.

Since aryl halides do not undergo nucleophilic substitution reactions easily, therefore, arylamines, *i.e.*, aromatic primary amines cannot be prepared by Gabriel phthalimide reaction.

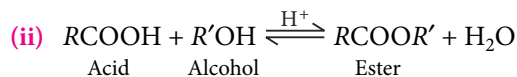


Propan-2-one on further oxidation gives a mixture of ethanoic acid and methanoic acid. Subsequent oxidation of methanoic acid gives CO_2 and H_2O .



22. (i) (a) Butanone < Propanone < Propanal < Ethanal
- This is due to increasing +I effect of alkyl group from ethanal to butanone which increases the electron density on carbonyl carbon and hence, attack by the nucleophile becomes slower and slower.
- (b) Acetophenone < *p*-Tolualdehyde < Benzaldehyde < *p*-Nitrobenzaldehyde
- This is due to :
- ketones are less reactive than aldehydes towards nucleophilic addition reactions.

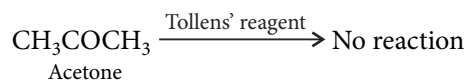
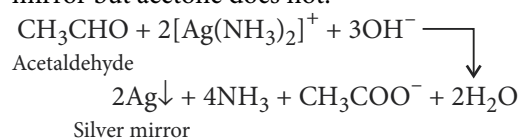
- CH_3 group increases the electron density on carbonyl carbon while nitro group decreases the electron density.



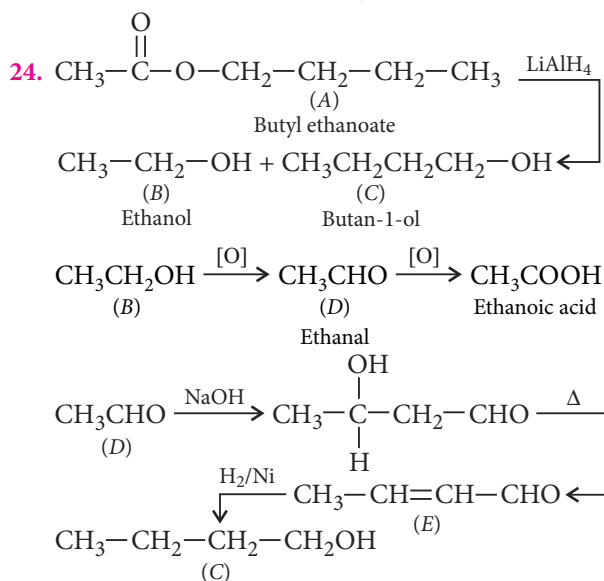
The esterification reaction is a reversible reaction. If water and the ester are allowed to remain in the reaction mixture the hydrolysis of the ester would take place. Hence, water or ester should be removed as soon as it is formed.

23. (i) Abhishek showed his concern and responsible nature by emphasizing that one should not play with chemicals in the laboratory.

- (ii) Acetaldehyde reduces Tollens' reagent to silver mirror but acetone does not.



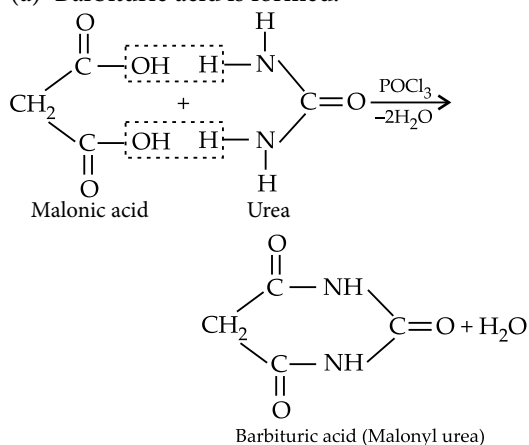
- (iii) Clemmensen reduction and Wolff-Kishner reduction.
- (iv) (a) Acetone is used as a solvent in industries.
(b) Acetone is used in the preparation of a number of chemicals such as chloroform ketene, acetic anhydride etc.



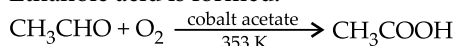
Hence (A) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$
 (B) $\text{CH}_3\text{CH}_2\text{OH}$
 (C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 (D) CH_3CHO
 (E) $\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$

OR

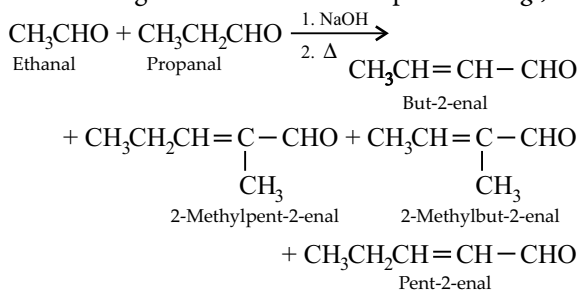
(i) (a) Barbituric acid is formed.



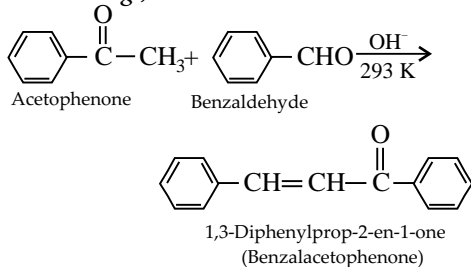
(b) Ethanoic acid is formed.



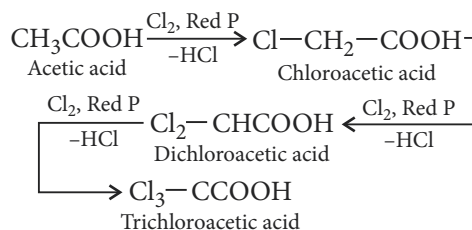
(ii) (a) Cross aldol condensation : When different aldehydes and ketones containing α -hydrogen atom are treated with dilute alkali, β -hydroxy aldehydes and ketones are formed. This reaction is called cross aldol condensation reaction. If both the reactants contain α -hydrogen atoms then it gives a mixture of four products. *e.g.*,



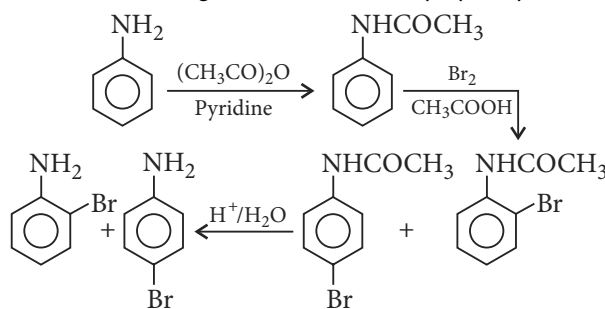
If only one carbonyl compound contains α -hydrogen then only one product is formed. *e.g.*,



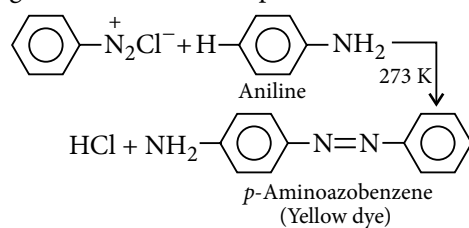
(b) Hell-Volhard-Zelinsky reaction: Carboxylic acids react with chlorine or bromine in the presence of red phosphorous to give compounds in which α -hydrogen atom is replaced by halogen atom.



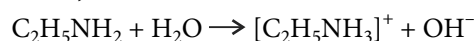
25. (i) Monobromoaniline can be prepared by first protecting the amino group by acetylation and then halogenation followed by hydrolysis.



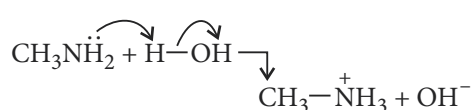
(ii) (a) Coupling reaction : It is the reaction of an aromatic diazonium salt with phenol or aromatic amine at low temperature to give coloured azo compounds.



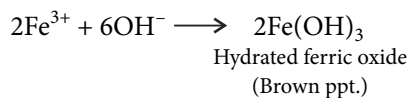
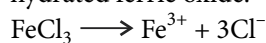
(b) Aqueous ethylamine is basic in nature because of the presence of free OH^- ions hence, it turns red litmus blue.



(c) Methylamine being more basic than water, accepts a proton from water liberating OH^- ions.

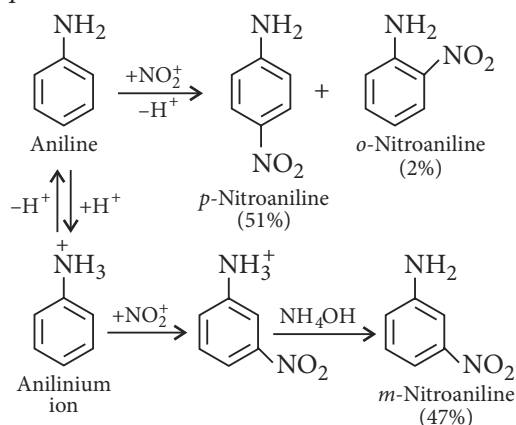


These OH^- ions combine with Fe^{3+} ions present in H_2O to form brown ppt. of hydrated ferric oxide.

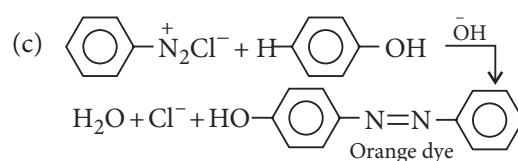
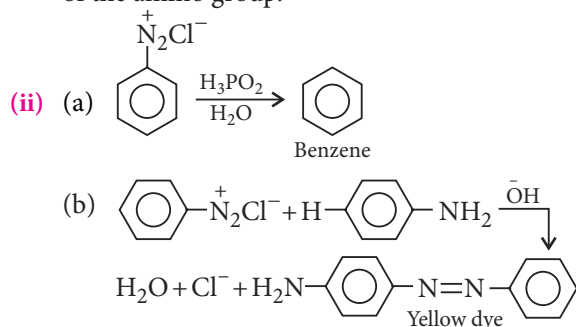


OR

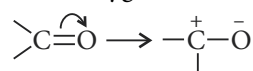
- (i) Nitration is usually carried out with a mixture of conc. HNO_3 + conc. H_2SO_4 (nitrating mixture). In presence of these acids, most of aniline gets protonated to form anilinium ion. Therefore, in presence of acids, the reaction mixture consists of aniline and anilinium ion. Now, $-\text{NH}_2$ group in aniline is *o,p*-directing and activating while the $-\text{NH}_3^+$ group in anilinium ion is *m*-directing and deactivating. Whereas nitration of aniline (due to steric hindrance at *o*-position) mainly gives *p*-nitroaniline, the nitration of anilinium ion gives *m*-nitroaniline. In actual practice, approx. 1 : 1 mixture of *p*-nitroaniline and *m*-nitroaniline is obtained.



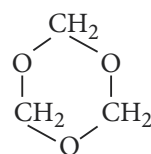
Thus, nitration of aniline gives a substantial amount of *m*-nitroaniline due to protonation of the amino group.



26. (i) In weakly acidic medium, the oxygen of the carbonyl group gets protonated which in turn by way of resonance increases the +ve charge on the carbonyl carbon. As a result, a nucleophile like ammonia derivative attacks it readily.
- (ii) Due to higher electronegativity, electron density shifts towards oxygen and carbon becomes electron deficient and acts as electrophilic centre and oxygen acts as nucleophilic centre.

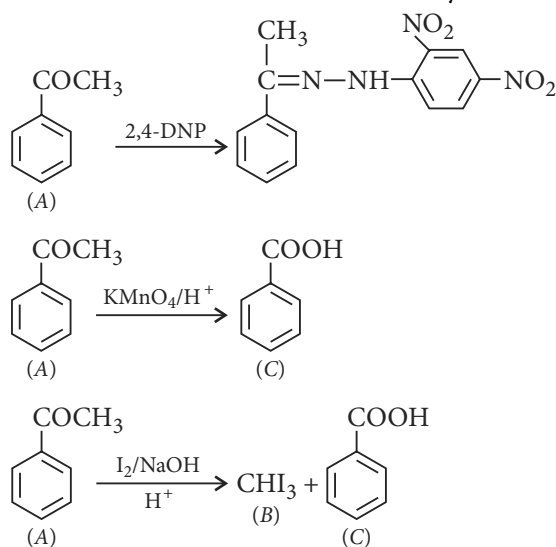


- (iii) 40% aqueous solution of methanal is called formalin and trioxane is a trimer of methanal.



OR

Molecular formula of the compound 'A' is $\text{C}_8\text{H}_8\text{O}$. As 'A' does not give Tollens' or Fehling's test, it must be a ketone. It gives positive test with 2, 4 - DNP and iodoform test. It means it is a methyl ketone.



EXAMINER'S MIND

CLASS XII



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

ALCOHOLS, PHENOLS AND ETHERS | ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

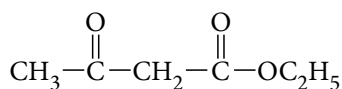
SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

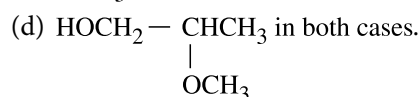
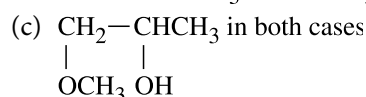
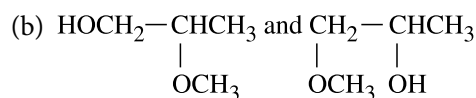
- Doctors detect diabetes disease by testing the glucose in urine by
(a) Nessler's solution (b) Fehling's solution
(c) Fenton's reagent (d) silver nitrate solution.
- Phenol is converted into bakelite by heating it with formaldehyde in the presence of an alkali or an acid. Which statement is true regarding this reaction?
(a) The electrophile in both cases is $\text{CH}_2=\text{O}$
(b) The electrophile in both cases is $\text{CH}_2=\text{OH}^+$
(c) The electrophile is $\text{CH}_2=\text{O}$ in the presence of an alkali and $\text{CH}_2=\text{OH}^+$ in the presence of an acid.
(d) It is a nucleophilic substitution reaction.

- The IUPAC name of the following compound is

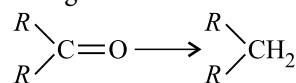


- (a) ethyl β -ketobutyrate
(b) ethyl-3-oxobutanoate
(c) 1-carbethoxypropanone
(d) ethyl acetoacetate.
- $$\text{Y} \xleftarrow[\text{CH}_3\text{ONa}]{\text{CH}_3\text{OH}} \text{H}_2\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{O} \end{array} \text{CHCH}_3 \xrightarrow[\text{H}^+]{\text{CH}_3\text{OH}} \text{X}$$

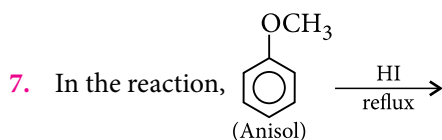
Here 'X' and 'Y' are respectively
(a) $\text{CH}_2-\underset{\text{OCH}_3}{\underset{|}{\text{CH}}}\text{CH}_3$ and $\text{HOCH}_2-\underset{\text{OCH}_3}{\underset{|}{\text{CH}}}\text{CH}_3$



- Which of the following reactions/reagents cannot be used for the given reduction reaction?

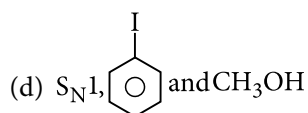
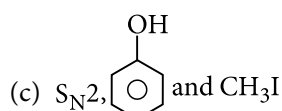


- (a) Clemmensen reduction
(b) Wolff-Kishner reduction
(c) HI/Red P at 200°C
(d) Wurtz reaction
- The order of reactivity of alcohols towards sodium metal is
(a) primary > secondary > tertiary
(b) primary < secondary < tertiary
(c) primary > secondary < tertiary
(d) primary < secondary > tertiary.



the mechanism followed and the major products are respectively

- (a) $\text{S}_{\text{N}}1$, $\text{C}_6\text{H}_5\text{OH}$ and CH_3I
(b) $\text{S}_{\text{N}}2$, $\text{C}_6\text{H}_5\text{I}$ and CH_3OH



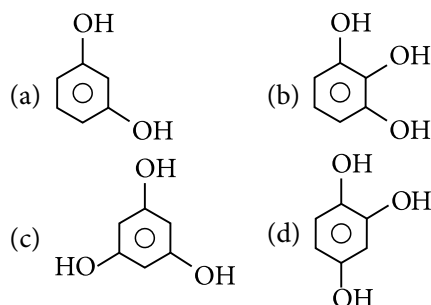
8. An organic compound 'X' on treatment with pyridiniumchlorochromate in dichloromethane gives compound 'Y'. Compound 'Y' reacts with I_2 and alkali to form triiodomethane. The compound 'X' is

- (a) C_2H_5OH (b) CH_3CHO
(c) CH_3COCH_3 (d) CH_3COOH

9. Friedel-Crafts acylation of benzene with benzoyl chloride gives

- (a) $C_6H_5COCH_3$ (b) CH_3COCH_3
(c) $C_6H_5COC_6H_5$ (d) none of these.

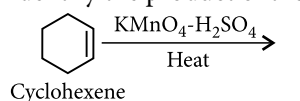
10. Which of the following compounds can react with hydroxylamine?



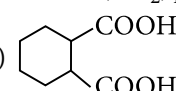
11. Ketones react with $Mg - Hg$ over water to give

- (a) pinacolones
(b) pinacols
(c) benzoquinone
(d) benzophenone.

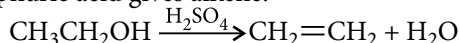
12. Identify the product of the following reaction :



Cyclohexene

- (a) $HOOC(CH_2)_4COOH$
(b) 
(c) $CH_3(CH_2)_4CH_3$
(d) $OHC(CH_2)_4CHO$

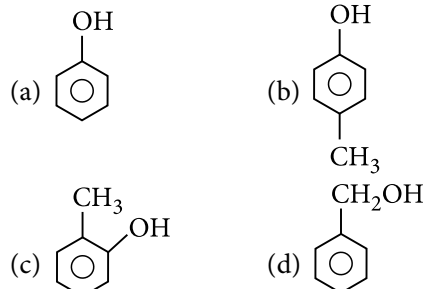
13. Dehydration of an alcohol in the presence of sulphuric acid gives alkene.



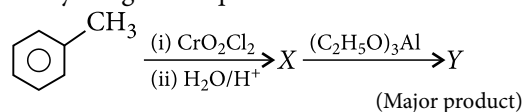
Here sulphuric acid acts as

- (a) an acid (b) a base
(c) a catalyst (d) all of these.

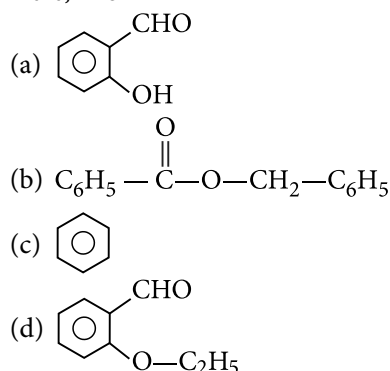
14. Which of the following will decolourise $KMnO_4/H^+$ and change the orange colour of $K_2Cr_2O_7/H^+$ to green?



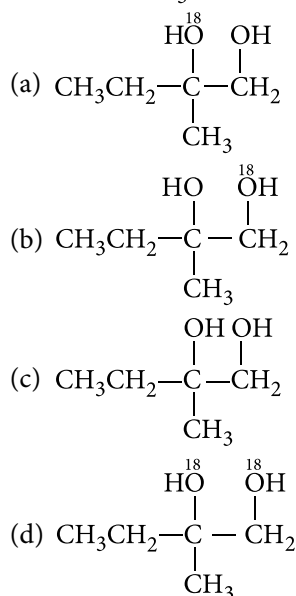
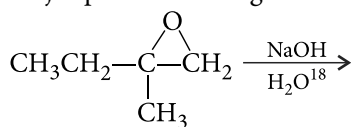
15. Study the given sequence of reactions :



Here, Y is



16. Major product of the given reaction is



17. Ozonolysis of 2,3-dimethylbut-1-ene gives

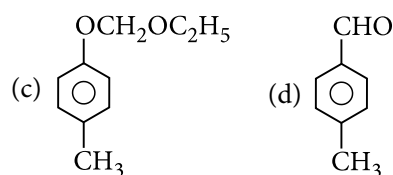
- (a) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 + \text{HCHO}$
 (b) $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 + \text{CH}_3\text{CHO}$
 (c) $\begin{matrix} \text{H}_3\text{C} \\ \diagup \\ \text{CH} \end{matrix} - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_3 + \text{CH}_3\text{CHO}$
 (d) $\begin{matrix} \text{H}_3\text{C} \\ \diagup \\ \text{CH} \end{matrix} - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_3 + \text{HCHO}$

18. *p*-Cresol reacts with chloroform in alkaline medium to give a compound 'A' which adds hydrogen cyanide to form the compound 'B'. Compound 'B' on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is

- (a)
- (b)
- (c)
- (d)

19. In the reaction, 'Z' is

- (a)
- (b)



20. Arrange the following compounds in decreasing order of reactivity towards nucleophilic addition reaction.

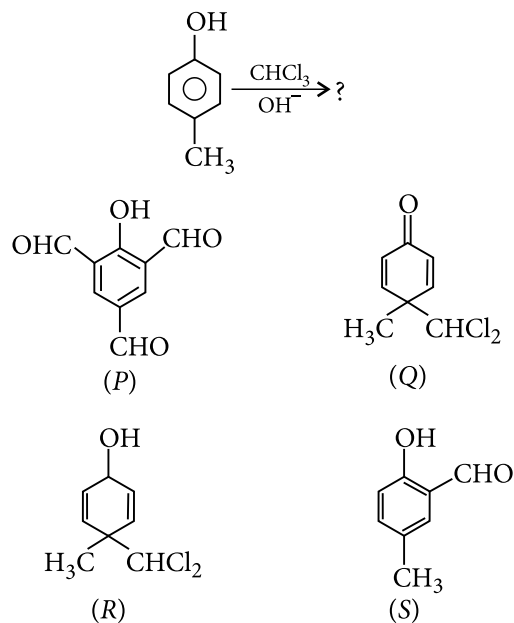
- Diethylketone (I) Benzaldehyde (II)
 Propanal (III) Acetaldehyde (IV)
 (a) I > II > III > IV (b) IV > III > II > I
 (c) II > III > I > IV (d) IV > III > I > II

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. In the following reaction, the product(s) formed is/are

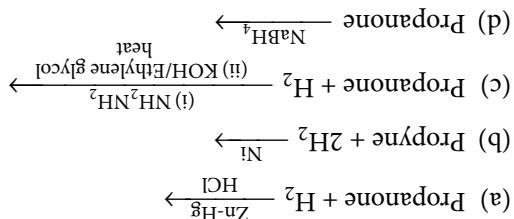


- (a) P (major) (b) Q (minor)
 (c) R (minor) (d) S (major)

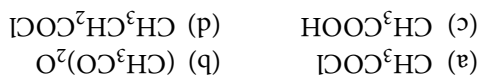
22. Which of the following cannot be prepared by the typical Williamson reaction?

- (a) R_3COCR_3
 (b) ArOAr
 (c) $\text{RCH}=\text{CHOCH}=\text{CHR}'$
 (d) $\text{C}_6\text{H}_5\text{CH}_2\text{OC}_2\text{H}_5$

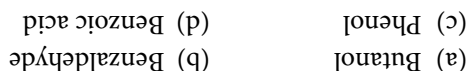
23. Which of the following reactions will yield propane?



24. Which of the following compounds can be used as an acylating agent?



25. Which of the following compounds will undergo reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid?



SECTION - III

Paragraph Type

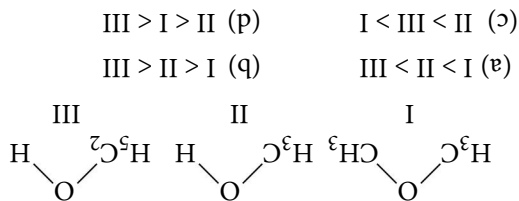
This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

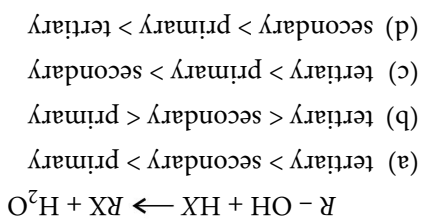
Alcohols and phenols consist of two parts, an alkyl/aryl group and a hydroxyl group. The properties of alcohols and phenols are chiefly due to the hydroxyl group. The nature of alkyl and aryl groups simply modify these properties.

26. Which of the following is most reactive towards aqueous HBr?

(a) 1-Phenyl-1-propanol
(b) 1-Phenyl-2-propanol
(c) 3-Phenyl-1-propanol
(d) None of these



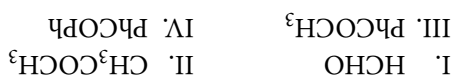
28. What is the order of reactivity of different types of alcohols in the reaction given below?



Paragraph for Questions 29 to 31

The aldehydes and ketones undergo nucleophilic addition reactions. A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon. The hybridisation of carbon changes from sp^2 to sp^3 in this process and a tetrahedral alkoxide intermediate is produced.

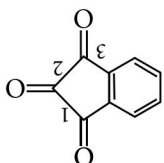
29. The increasing order of the rate of HCN addition to the given compounds is



30. Which of the following is an example of nucleophilic addition?

(a) $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{CH}_3 \xrightarrow{\text{NH}_2\text{NH}_2, \text{H}^+} \text{C}_6\text{H}_5-\text{C}(=\text{NNH}_2)-\text{CH}_3$
(b) $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{CH}_3 \xrightarrow{\text{LiAlH}_4} \text{C}_6\text{H}_5-\text{CH}_2-\text{OH}$
(c) Both (a) and (b)
(d) None of these

31. Which carbonyl group of the given compound is most reactive for nucleophilic addition reaction?



- (a) 1
(b) 2
(c) 3
(d) All have equal reactivity.

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- 32.** Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the codes given below the lists:

List I	List II
P.	1. (i) $\text{Hg}(\text{OAc})_2$, (ii) NaBH_4
Q.	2. NaOEt
R.	3. $\text{Et} - \text{Br}$
S.	4. (i) BH_3 ; (ii) $\text{H}_2\text{O}_2 / \text{NaOH}$

P	Q	R	S
(a) 2	3	1	4
(b) 3	2	1	4
(c) 2	3	4	1
(d) 3	2	4	1

- 33.** Match the starting materials given in List I with the products formed by these with HI given in List II and select the correct answer using the codes given below the lists :

List I	List II
P. $\text{CH}_3 - \text{O} - \text{CH}_3$	1. + CH_3I
Q.	2. + CH_3OH
R.	3. $\text{CH}_3 - \text{OH} + \text{CH}_3 - \text{I}$
S.	4. + CH_3I

	P	Q	R	S
(a)	1	2	3	4
(b)	4	3	2	1
(c)	3	4	2	1
(d)	3	4	1	2

- 34.** Match the reactions given in List I with the suitable reagents given in List II and select the correct answer using the codes given below the lists :

List I	List II
P. Benzophenone \rightarrow Diphenylmethane	1. LiAlH_4
Q. Benzaldehyde \rightarrow 1-Phenylethanol	2. DIBAL—H
R. Cyclohexanone \rightarrow Cyclohexanol	3. $\text{Zn-Hg}/\text{Conc. HCl}$
S. Phenyl benzoate \rightarrow Benzaldehyde	4. CH_3MgBr

	P	Q	R	S
(a)	3	4	1	2
(b)	4	3	1	2
(c)	1	2	4	3
(d)	1	3	2	4

SECTION - V

Assertion Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.

- 35. Assertion :** Reimer-Tiemann reaction of phenol with CCl_4 in NaOH at 340 K gives salicylic acid as the major product.

Reason : The reaction occurs through intermediate formation of dichlorocarbene.

- 36. Assertion :** With HI at 373 K, methyl *tert*-butyl ether gives *tert*-butyl iodide and methanol.

Reason : The reaction occurs by $\text{S}_{\text{N}}2$ mechanism.

- 37. Assertion :** Claisen condensation of $\text{CH}_3 - \text{COOC}_2\text{H}_5$ (on heating with $\text{C}_2\text{H}_5\text{ONa}$) produces ethyl acetoacetate.

Reason : Ethyl acetoacetate gives the tests of $\text{—}\overset{\text{O}}{\parallel}\text{C—}$ and $\text{—COOC}_2\text{H}_5$ functional groups only.

38. Assertion : Acetaldehyde on treatment with alkali gives aldol.

Reason : Acetaldehyde molecule contains α -hydrogen atom.

39. Assertion : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

40. Assertion : pK_a value of phenol is lower than that of ethanoic acid.

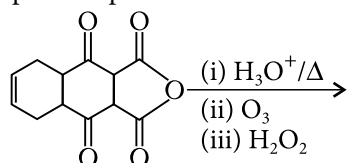
Reason : Phenoxide ion is more resonance stabilised than $RCOO^-$ ion.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

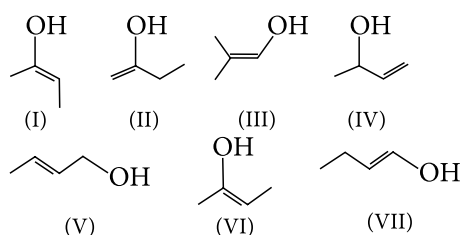
41. In the given reaction, the total number of carboxylic groups in the product is



42. When ethanal reacts with propanal in the presence of a base, the number of products formed is

43. When Glucose, $[OHC(CHOH)_4CH_2OH]$ is oxidised with periodic acid, number of moles of formic acid obtained by one mole of glucose is

44. In the given list of compounds, number of compounds which are enol forms of 2-butanone is



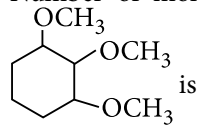
45. Acetylation of a polyhydric alcohol increases its molecular mass by 126 units. The number of 'OH' groups in the molecule is

46. Number of isomers of $C_5H_{11}OH$ which are primary alcohols is

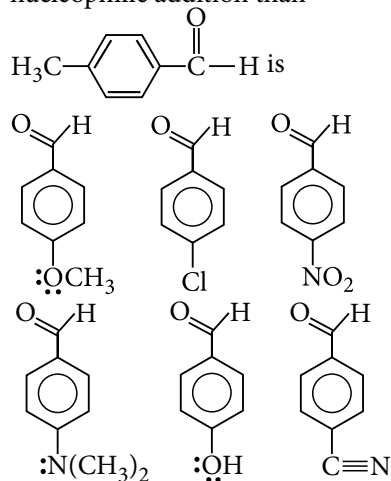
47. Number of products formed by 1, 2-diethylbenzene on ozonolysis is

48. Number of alcohols which are chiral in nature with molecular formula $C_4H_{10}O$ are

49. Number of moles of 'HI' which will react with



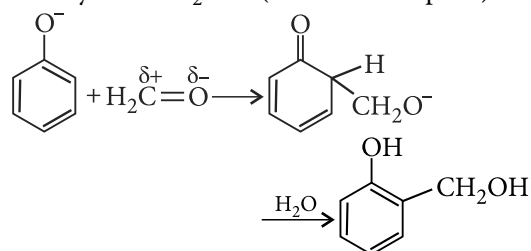
50. From the following compounds, the number of compounds which show(s) higher rate of nucleophilic addition than



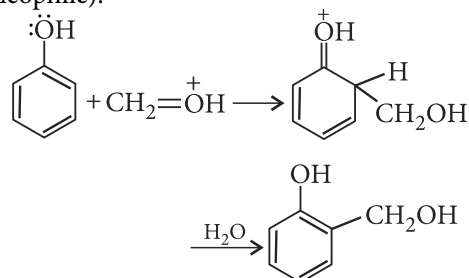
SOLUTIONS

1. (b): Simple sugars e.g., glucose give a positive test with Fehling's solution thus it is used to test the presence of glucose in urine for detecting diabetes.

2. (c): Condensation of phenol with formaldehyde is an electrophilic substitution reaction. Base converts phenol into phenoxide ion which being more reactive, reacts easily with $CH_2=O$ (a weak electrophile).

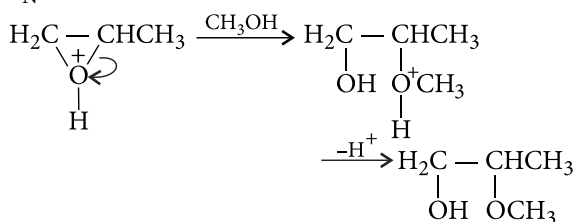


In presence of an acid, $CH_2=O$ (a weak electrophile) is protonated to $CH_2=OH^+$ (a strong electrophile) which easily reacts with phenol (a weak nucleophile).

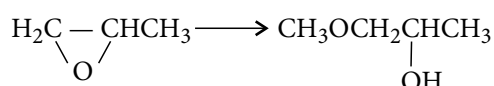


3. (b)

4. (b): In the acid-catalysed ring opening of an unsymmetrical epoxide, the nucleophile attacks primarily at the more substituted carbon atom because such atom of the protonated epoxide acquires a considerable positive charge. This resembles a more stable 2° or 3° carbocation and hence, the reaction is S_N1 like.

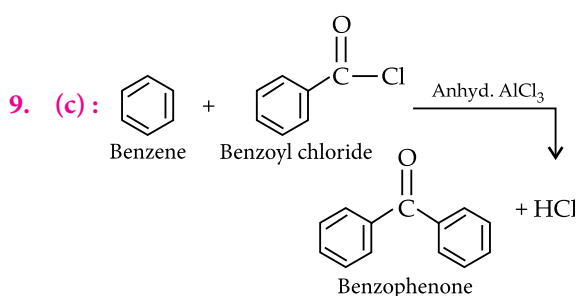
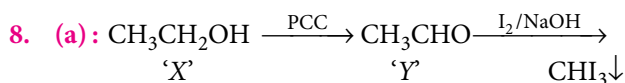
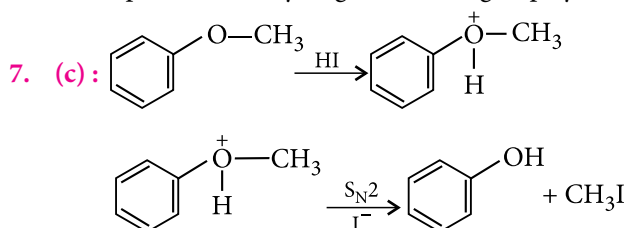


In case of CH₃ONa, —OCH₃ being a strong nucleophile, opens the strained epoxide ring in a direct S_N2 reaction, i.e., by attacking at the least hindered carbon atom.

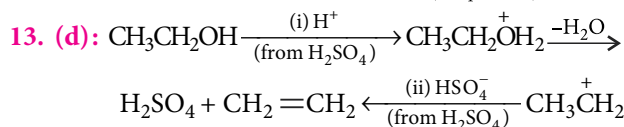
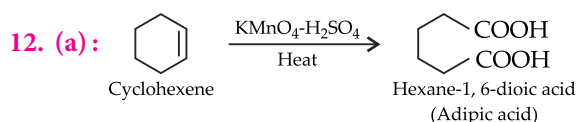
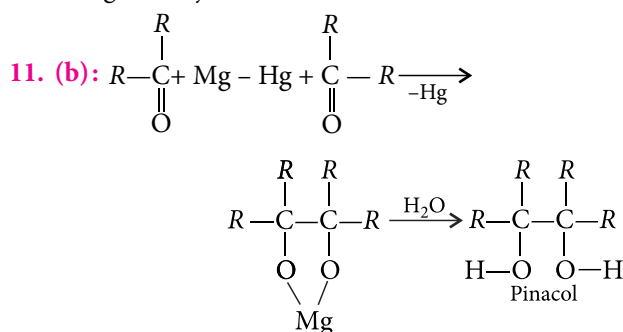


5. (d): Wurtz reaction cannot be used for this reduction.

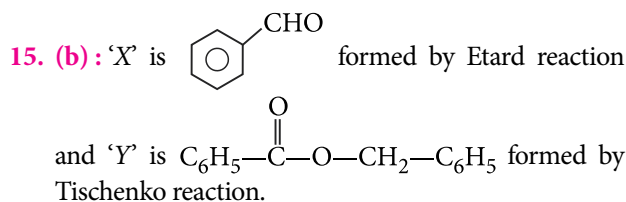
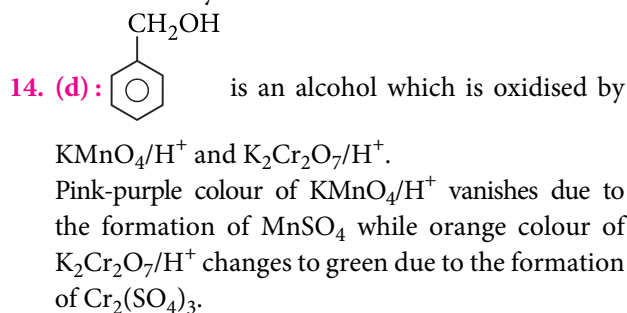
6. (a): Due to +I effect of alkyl groups, the O—H bond in tertiary alcohols is the strongest and hence most difficult to break followed by the O—H bond in secondary alcohols while the O—H bond in primary alcohols is the weakest. Lower the degree of alcohol, higher is the acidic character and easier is the displacement of hydrogen of —OH group by Na.



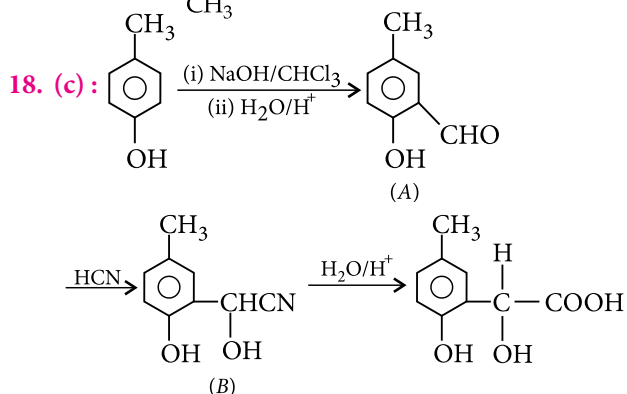
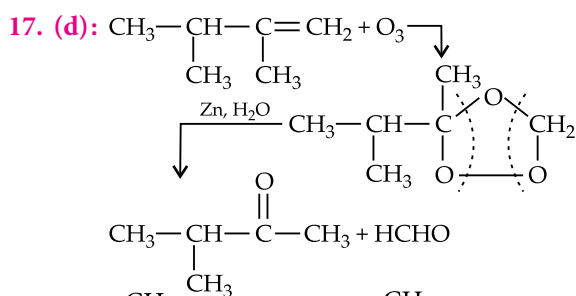
10. (c): We know that phenols show keto-enol tautomerism and the stability of the keto form depends upon the number of keto groups. More the number of keto groups, higher will be stability of the keto tautomer. Thus trihydric phenols should exist in keto form in considerable amount but only when the two keto groups are not on adjacent carbon atoms which decreases stability due to positive charge on adjacent carbon atoms.



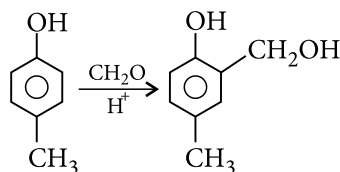
H₂SO₄ is acting as an acid in step (i) and a base in step (ii). Since it is regenerated back as such, it also acts as a catalyst.



16. (b): Base catalysed epoxide opening is a typical S_N2 reaction in which attack of the nucleophile takes place at the less hindered epoxide.



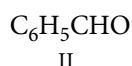
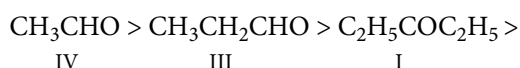
19. (b): $\text{CH}_2(\text{OC}_2\text{H}_5)_2$ is an acetal of formaldehyde with ethanol. In presence of an acid, it decomposes to CH_2O and $\text{C}_2\text{H}_5\text{OH}$.



20. (d): Ketones are less reactive than aldehydes due to the presence of two large electron releasing alkyl groups, which hinder the attack of nucleophile on the carbonyl carbon and also reduces the electrophilicity of the carbonyl carbon.

As the size of the alkyl group increases, +I effect increases and thus reactivity decreases. Aromatic aldehydes and ketones are less reactive due to +R effect of the benzene ring.

Thus, the decreasing order of reactivity towards nucleophilic addition reaction is :



21. (b, d) : It is Reimer-Tiemann reaction.

22. (a, b, c) : *tert*- and *sec*-carbocations are liable to undergo elimination reaction in presence of strong alkoxide bases. Aryl and vinyl halides do not undergo nucleophilic substitution.

23. (a, b, c) : (a) is Clemmensen reduction.

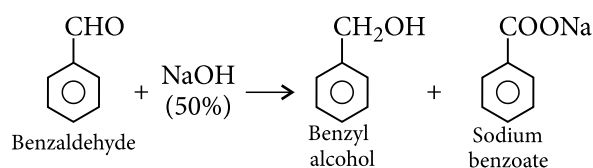
(b) is catalytic reduction.

(c) is Wolff-Kishner reduction.

(d) Ketones with sodium borohydride give secondary alcohols.

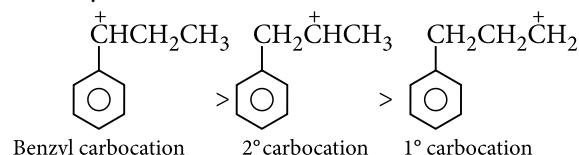
24. (a, b, d) : Stronger the basic nature of the leaving group, weaker will be its leaving ability. In CH_3COOH , OH^- is a strong base so it cannot be removed easily to form CH_3CO^+ required for acylation.

25. (b) : It is Cannizzaro reaction.



26. (a) : Carbocation is formed as an intermediate hence, the species capable of forming most stable carbocation will be most reactive.

Stability of carbocation follows the order :

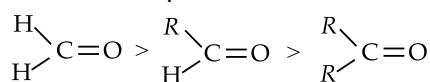


27. (c)

28. (a) : Reaction of alcohols involving cleavage of C—OH bond follows the reactivity order : Tertiary > secondary > primary, according to the stability of carbocation intermediate.

29. (c) : Addition of HCN to carbonyl compounds is a characteristic nucleophilic addition reaction of carbonyl compounds.

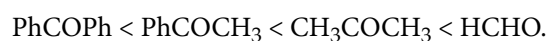
Order of reactivity :



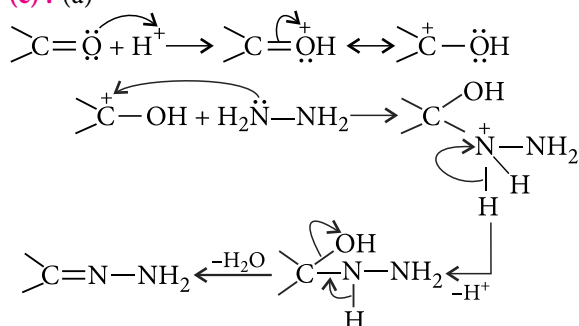
The lower reactivity of ketones over aldehydes is due to +I effect of the alkyl (R) group and steric hindrance. As the size of the alkyl group increases, the reactivity of the ketones further decreases.

The aromatic aldehydes and ketones are less reactive than their aliphatic analogues. This is due to the +R effect of the benzene ring.

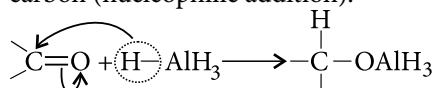
Hence, the increasing order of the rate of HCN addition to compounds HCHO , CH_3COCH_3 , PhCOCH_3 and PhCOPh is



30. (c) : (a)



(b) In the reduction of carbonyl group with LiAlH_4 or NaBH_4 , a hydride ion is transferred from the metal to the carbonyl carbon (nucleophilic addition).



31. (b)

32. (a)

P : 3° Chloro compound is converted to ethene by EtONa .

Q : It is Williamson synthesis giving ether by EtBr .

R : It is Markovnikov's addition by oxymercuration demercuration.

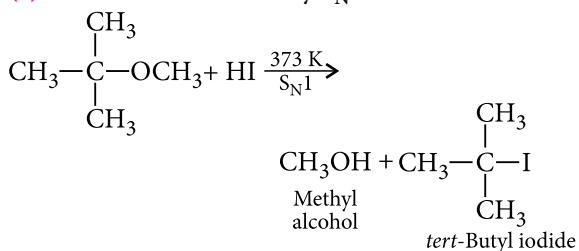
S : It is hydroboration oxidation which lead to anti-Markovnikov's addition.

33. (c)

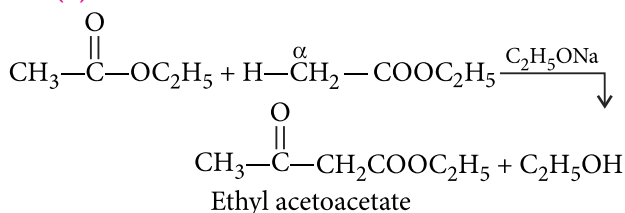
34. (a)

35. (c) : Nucleophilic attack of phenolate ion through the *ortho*-carbon atom occurs on CCl_4 (a neutral electrophile) to form an intermediate which on hydrolysis gives salicylic acid.

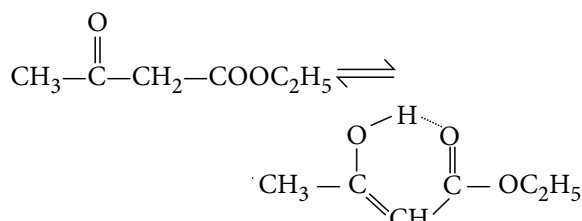
36. (c) : The reaction occurs by $\text{S}_{\text{N}}1$ mechanism :



37. (b) :

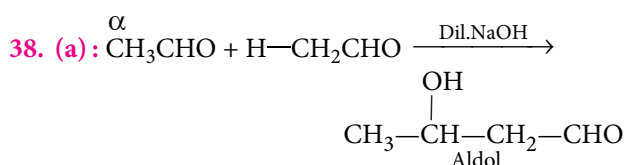


It exists as :



Ethyl acetoacetate gives the test of four groups —OH,

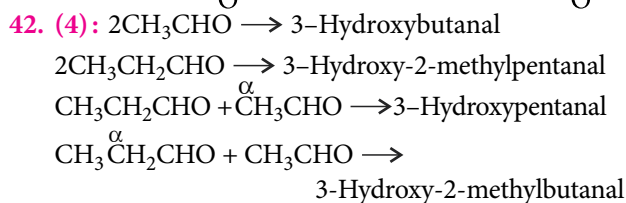
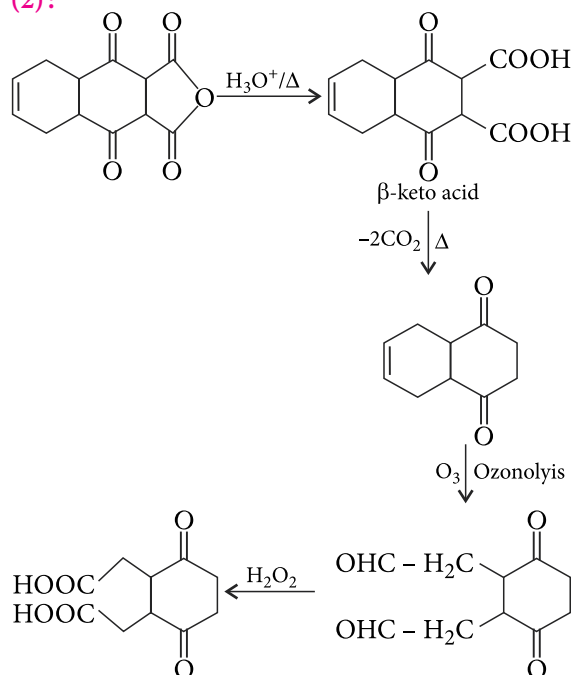
$\text{C}=\text{C}$, $-\overset{\text{O}}{\parallel}{\text{C}}-$ and $-\text{COOC}_2\text{H}_5$.

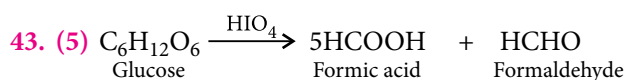


39. (c) : Aromatic aldehydes and formaldehyde do not contain α -hydrogen atom and thus, undergo cannizzaro reaction. Formaldehyde is more reactive than aromatic aldehydes.

40. (d) : Phenol is less acidic than acetic acid and has higher pK_a value than that of CH_3COOH .

41. (2) :



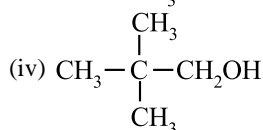
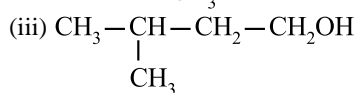
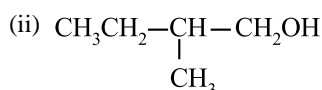


44. (3): I, II and VI are enol tautomers of 2-butanone.

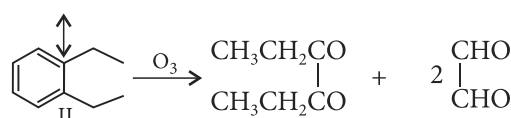
45. (3): Acetylation of alcohol increases the mass by 42 units per —OH group.

$$\text{No. of —OH groups} = \frac{\text{Increase in mass}}{42} = \frac{126}{42} = 3$$

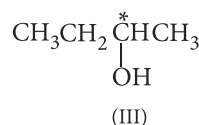
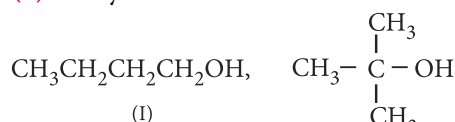
46. (4): (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$



47. (3): 1, 2-Diethylbenzene is a resonance hybrid of the two structures which on ozonolysis give three different products.



48. (1): Only one alcohol contains chiral carbon atom.



Only III is chiral in nature.

49. (6)

50. (3)



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 YOUR WAY CBSE XI



Contd. from page no.23

(i) (a) The typical reactions of benzene are electrophilic substitution reactions. Higher the electron density in the benzene ring, more reactive is the compound towards these reactions. Since, —NO₂ is a more powerful electron withdrawing group than —Cl, therefore, more the number of nitro groups, less reactive is the compound. Thus, the overall reactivity decreases in the order :

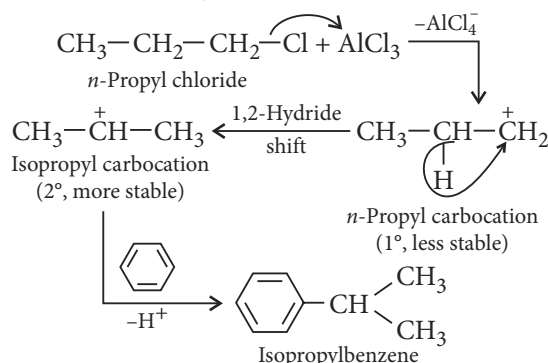
Chlorobenzene > *p*-nitrochlorobenzene
 > 2, 4-dinitrochlorobenzene

(b) Here, —CH₃ group is electron donating but —NO₂ group is electron withdrawing. Therefore, the maximum electron-density will be in toluene, followed by *p*-nitrotoluene followed by *p*-dinitrobenzene. Thus, the overall reactivity decreases in the order :

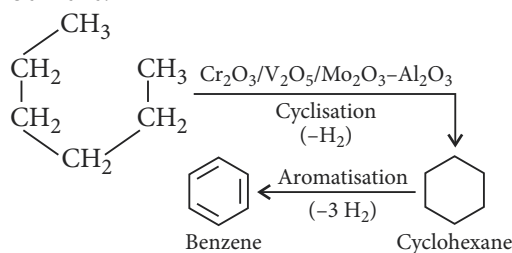
Toluene > *p*-nitrotoluene > *p*-dinitrobenzene

(ii) During Friedel-Crafts reaction, carbocation is the intermediate. Therefore, anhy. AlCl₃ first reacts with *n*-propyl chloride to form *n*-propyl cation. This being 1° is less stable and hence, rearranges to the more stable 2° carbocation,

i.e., isopropyl carbocation by hydride shift. The isopropyl carbocation then reacts with benzene to form isopropylbenzene.



(iii) When vapours of hexane are passed over heated catalyst consisting of Cr₂O₃, Mo₂O₃, and V₂O₅ supported over Al₂O₃ at 773 K under 10-20 atm pressure, cyclisation and aromatisation occur simultaneously to give benzene.





ADVANCED CHEMISTRY BLOC

(OXIDATION STATES OF *d*-BLOCK ELEMENTS AND LANTHANIDES)

Mukul C. Ray, Odisha

Oxidation States of 3*d*-Series Elements

On moving across the 3*d*-series, the nuclear charge increases at each stage with addition of one proton to the nucleus. Also, inner core electrons increase as electrons enter into 3*d*-subshell. The outermost shell for these elements are the 4*s*-electron(s). The 3*d*-electrons do not screen the nuclear charge more effectively as the 3*d*-orbitals are diffused in shape. As a consequence, the effective nuclear charge increases and 3*d*-electrons experience more and more nuclear charge. They become progressively more stabilised across the series. In other words, as the nuclear charge increases, the energy of 3*d*-electrons falls well below that of 4*s* electrons and the elements in the later half of the series typically exhibit oxidation state of II, which corresponds to removal of only two 4*s*-electrons. Higher oxidation states of these elements are produced with difficulty. Following are the distinguished points :

- Ti(II), V(II) and Cr(II) are good reducing agents as they have tendency to lose 3*d*-electrons. On moving towards right in the series, the 3*d*-electrons become more stable and are reluctant to be lost.
- Mn(VII), Cr(VI), V(V) oxidation states exist as permanganate, dichromate or chromate and vanadate respectively. These high oxidation states are the results of loss of 3*d*-electrons. Since 3*d*-electrons become increasingly stable, these ions have a tendency to fill their *d*-orbitals and hence they act as oxidising agents. The oxidising ability increases as expected in the order :
$$V(V) < Cr(VI) < Mn(VII).$$
- These elements form compounds in lower oxidation states of (I), (0) and even negative with pi acid ligands (a part of coordination complexes). Cu(I) compounds are relatively stable due to 3*d*¹⁰ configuration.
- Mainly ionic compounds are formed by all elements except Sc in the oxidation state II. The oxides are

basic and the halides are ionic. With increase in the atomic number, the divalent state becomes more stable.

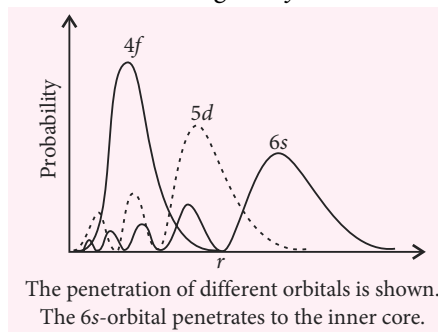
- Oxidation state III is exhibited by all the elements except Zn. Sc(III) is very stable whereas Cu(III) is highly oxidising.
- Oxidation state IV is important only for Ti and V, while for the rest of the elements, it is found only in oxo and fluoro complexes.

Oxidation States of *d*-Block Elements

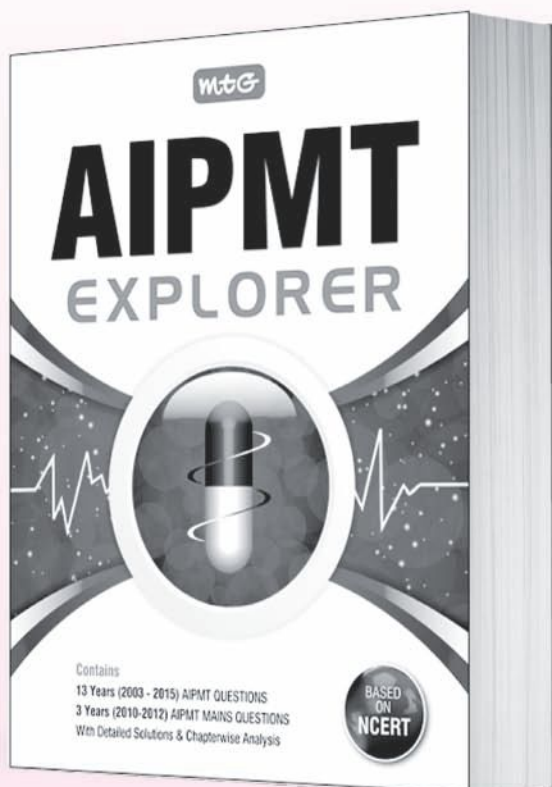
As the atomic number increases, the energy of all orbitals tends to fall. The difference in penetrating power now plays the key role. The *s*-orbital is compact but *d*-orbital is diffused. Both feel contracted but *d*-orbital experiences more contraction. As a result, when we move down the group, the energy gap between *ns*- and (*n* – 1)*d*-orbitals decreases. Now, both these kind of electrons are available towards bonding under similar circumstances. So higher oxidation states now become more probable. Iron fails to show VIII oxidation state, whereas osmium in the same group shows VIII oxidation state in OsO₄.

Oxidation States of Inner Transition Elements

The lanthanides are those elements in which the 4*f*-orbitals are gradually filled. At lanthanum, the 5*d*-orbital is lower in energy than 4*f*-orbital. As more protons are added to the nucleus, the 4*f*-orbitals contract rapidly and become more stable than the 5*d*-orbitals and electrons start entering the 4*f*-orbital.



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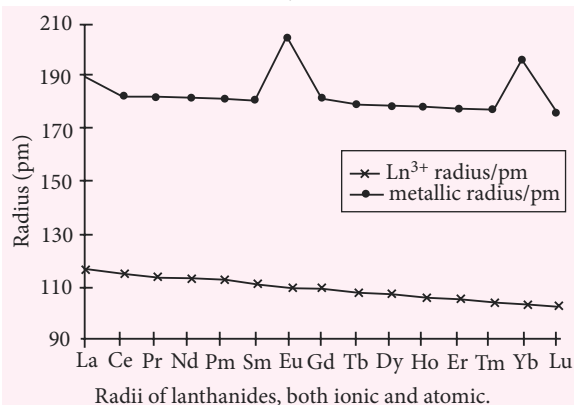
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Along the series, there is a decrease in both the atomic and ionic radii of the Ln^{3+} ions. The $4f$ -electrons are inside the $5s$ - and $5p$ -electrons and are core-like in their behaviour being shielded from the bonded groups. The $5s$ - and $5p$ -orbitals and also the $6s$ -orbitals penetrate the $4f$ -subshell and are not shielded from increasing nuclear charge and hence, because of the increasing effective nuclear charge, they contract as the atomic number increases. Lanthanide contraction is sometimes spoken as if it were unique. But similar phenomena also exists like actinide contraction, scandide contraction. The abrupt increase in atomic size for europium and ytterbium is because they donate only two electrons (associated with stability of half filled and fully filled orbitals) whereas others donate three electrons to the electron pool of metallic crystal.



Now, it can be concluded that III is the most common oxidation state of lanthanides both in solid state and in aqueous solutions. Lattice energy in solid state and hydration energy in aqueous solution are so adjusted that they support III oxidation state for lanthanides. The notables points are :

- The III oxidation state is generally the more stable for Ln.
- Other oxidation states are available, especially if a $4f^0$, $4f^7$ and $4f^{14}$ configuration results.
- The most accessible $2+$ ions are Eu^{2+} ($4f^7$) and Yb^{2+} ($4f^{14}$).
- The most accessible $4+$ ions are Ce^{4+} ($4f^0$) and Tb^{4+} ($4f^7$).

In actinides, the energy gap between $5f$ -orbital and $7s$ -orbital decreases. The $5f$ -electrons are now easily available for bonding. They are not deeply seated as $4f$ -electrons. Hence, actinides show higher oxidation states. Uranium, for example shows VI oxidation state. The highest oxidation state shown by any actinide is VII.

As the $4f$ -electrons are deeply held, the magnetic properties of lanthanides are largely independent of environment. In case of actinides, the magnetic properties are highly complex.

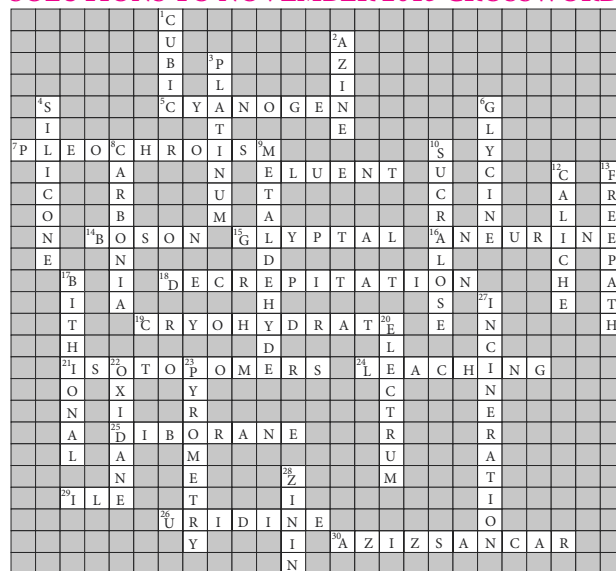


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SOLUTIONS TO NOVEMBER 2015 CROSSWORD



Winners of November 2015 Crossword

- Manju Rana (Uttar Pradesh)
- Ritesh Rao (Karnataka)



NEWS CORNER



Bhutan to pave 'green' roads with plastic

Bhutan has come up with a new way to pave its roads : waste plastic. As part of efforts to curb the use of fossil fuels and deal with growing amounts of plastic waste, the country plans to mix used plastic bottles and other waste plastic with bitumen to blacktop its roads.

The Green Road public private project is expected to reduce the amount of bitumen imported from India by 40% and cut the amount of plastic waste going into landfills by 30-40% said plastic road entrepreneur Rikesh Gurung.

Although only 10 to 15% of the mix used to pave roads is plastic, the project is expected to consume all the plastic waste in the country of over 7,80,000 people, Gurung said.

"We will use the plastic waste to build eco-friendly and durable roads..." said the 30-year-old, who in October built an initial 150-metre length of pilot road in the capital, Thimphu.

"Recycling plastic waste and not burning (it) is the correct approach to protect the environment," he said. Gurung came across the idea of using plastic waste in blacktopping roads when he was studying at Thiagarajar College of Engineering in India's Madurai.

Acid fog dissolved rocks on Mars

Mars has acid fog which eats away rocks and is caused by volcanic eruptions on the red planet, a new study suggests.

A planetary scientist has found how acidic vapours may have eaten at the rocks in a 100-acre area on Husband Hill in the Columbia Hills of Gusev Crater on Mars. Shoshanna Cole's research focused on the 'Watchtower Class' outcrops on Cumberland Ridge and the Husband Hill summit. "The special thing about Watchtower Class is that it's very widespread which means that the rocks record environments that existed on Mars billions of years ago," she said.

By combining data from previous studies of the area on Mars, Cole saw some intriguing patterns emerge. Spirit examined Watchtower Class rocks and the chemical composition of these rocks, as determined by Spirit's Alpha Proton X-ray Spectrometer, is the same, but the rocks looked different to all of the other instruments.



New insulin pill may replace jabs

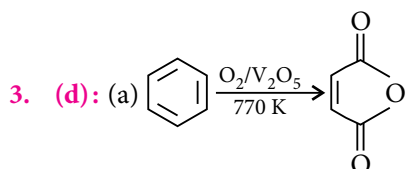
Indian-origin scientists are developing a patch for diabetics that attaches to the intestinal wall and releases insulin after being swallowed in the form of a pill. Existing marketed insulin formulations are injectables -currently, it is not possible for insulin to be taken by mouth. Samir Mitragotri, a professor in the college of engineering at the University of California Santa Barbara, and Amrita Banerjee, a postdoctoral fellow, developed patches made of mucoadhesive polymers loaded with insulin and an intestinal permeation enhancer, then placed the patch devices in enteric-coated capsules.

Courtesy : The Times of India

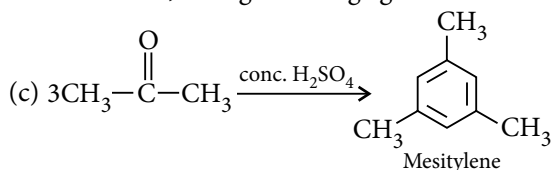
CHEMISTRY MUSING

SOLUTION SET 28

- (d): $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{I}_2$
 $3\text{I}_2 + 6\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow 3\text{Na}_2\text{S}_4\text{O}_6 + 6\text{NaI}$
 $1 \text{ mol K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{KI}} 3 \text{ mol I}_2 \equiv 6 \text{ mol Na}_2\text{S}_2\text{O}_3$
- (d): (a) Extensive properties depend on the mass of substance.
 (b) If expressed in terms of per mole, the mass of substance is fixed so for one mole of substance it remains same.
 (c) Extensive property depends upon two variables and number of moles in case of solution of two substances.

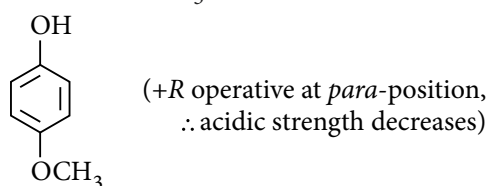
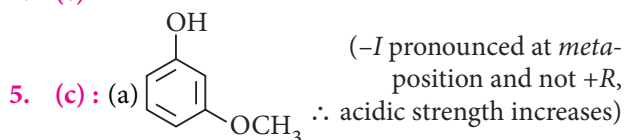


(b) HI formed as a byproduct, is very strong reducing agent which can convert $\text{C}_6\text{H}_5\text{—I}$ back to benzene. Thus, strong oxidising agent is used.



(d) π -electrons are delocalised in benzene hence, it does not decolourise bromine water.

4. (c)



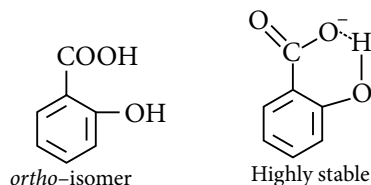
(b) $-R$ groups increase the acidic strength so, *ortho* and *para*-nitrobenzoic acids are more acidic. Also, *ortho*-nitrobenzoic acid is more acidic than *para*-isomer due to *ortho* effect. In *meta*-isomer only, $-I$ effect is operative, so it is less acidic than *ortho* and *para*-isomers.
 (c) Lesser the charge density, more stable is the base. The stability of conjugate base is

$$\text{F}^- > \text{OH}^- > \text{CH} \equiv \text{C}^- > \text{NH}_2^-$$

Hence, the order of acidic strength is

$$\text{HF} > \text{H}_2\text{O} > \text{CH} \equiv \text{CH} > \text{NH}_3$$

(d) Hydroxybenzoic acids: $-\text{OH}$ group is a $+R$ group so acidic strength of benzoic acid should decrease but in *ortho*-isomer, the conjugate base is highly stable due to intramolecular H-bonding.



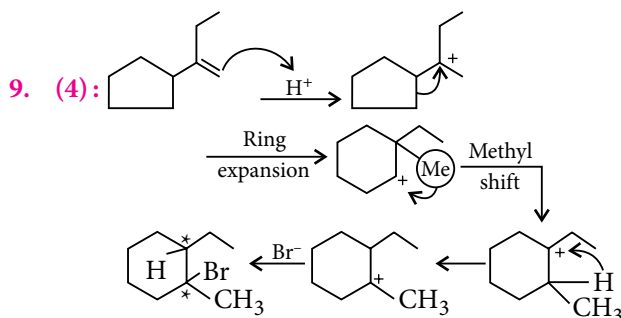
In *meta*-isomer, $-I$ effect increases acidic strength whereas in *para*-isomer, $+R$ effect dominates and its acidic strength is less than that of the benzoic acid.

6. (c)

7. (c): $Z = \frac{PV}{RT}$

If values of critical constants are used, $Z = \frac{P_c V_c}{RT_c} = \frac{3}{8}$

8. (c): $Z < 1$ i.e., $PV < nRT$ and attractive forces are dominating. Therefore, gram molar volume will be less than 22.4 L at STP.



10. (4): $\frac{p_{\text{H}_2\text{O}}}{p_{\text{C}_6\text{H}_5\text{NO}_2}} = \frac{W_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} \times \frac{M_{\text{C}_6\text{H}_5\text{NO}_2}}{W_{\text{C}_6\text{H}_5\text{NO}_2}}$

$$p_{\text{H}_2\text{O}} = 733 \text{ mm Hg}, p_{\text{C}_6\text{H}_5\text{NO}_2} = 27 \text{ mm Hg},$$

$$M_{\text{H}_2\text{O}} = 18 \text{ g mol}^{-1}, M_{\text{C}_6\text{H}_5\text{NO}_2} = 123 \text{ g mol}^{-1}$$

$$\frac{W_{\text{H}_2\text{O}}}{W_{\text{C}_6\text{H}_5\text{NO}_2}} = \frac{733}{27} \times \frac{18}{123} = 3.972 \approx 4$$



Solution Senders of Chemistry Musing

SET 28

- Manmohan Krishna (Patna)
- Debdutta Bose (West Bengal)
- Shreya Sharma (Ambala)

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YOU ASK WE ANSWER

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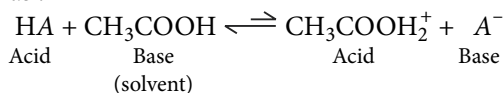
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The best questions and their solutions will be printed in this column each month.

Q1. Is it possible for a strong acid like HNO_3 to act as a proton acceptor? If yes, please mention the conditions.

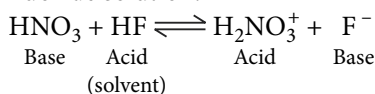
(Udit Mahajan, Chandigarh)

Ans. The capacity of an acid to donate protons depends upon the base strength of the solvent which acts as the proton acceptor. For example, in acetic acid the ionisation of a strong acid HA can be represented as :



The equilibrium cannot lie much to right since acetic acid has small tendency to accept proton. Therefore, even the strong acids ionise feebly in acetic acid.

However, in hydrogen fluoride, which has no proton accepting tendency at all even the strongest acid is incapable of acting as a proton donor. Thus, nitric acid will ionise slightly as a base in hydrogen fluoride solution.



Q2. I have seen in laboratory, that pure lead and pure zinc do not dissolve in acid solutions easily but do so if air is bubbled through the solution. Please explain the reason.

(Sanket Aggarwal, Delhi)

Ans. The standard electrode potential (E°) of lead is -0.13 volt. It should, therefore, dissolve readily in dilute hydrochloric acid, evolving hydrogen. Zinc ($E^\circ = -0.76$ volt) should do so even much more readily. However, in actual practice, neither lead

nor pure zinc dissolves in hydrochloric acid and no evolution of hydrogen occurs. This is because of hydrogen overvoltage. The bubble overvoltage of hydrogen over lead is 0.64 volt and that over zinc is 0.70 volt.

In the presence of an oxidising agent like oxygen (air), pure lead or zinc gets oxidised but there may be no evolution of hydrogen gas as it may get oxidised as soon as formed. Similarly, zinc (or any other base metal like lead, iron, etc.) will dissolve easily when it contains other metal having low hydrogen overvoltage as an impurity. In such a case, zinc dissolves producing Zn^{2+} ions while hydrogen is liberated on the impurity part of the zinc rod itself.

Q3. Recently read in newspaper that processed or red meat can cause cancer. Explain.

(Aradhita Roy, West Bengal)

Ans. *N*-Nitrosamines are very powerful carcinogens which scientists fear may be present in many foods, especially in cooked meats that have been cured with sodium nitrite.

Sodium nitrite is added to many meats (e.g., bacon, ham, frankfurters, sausages, and corned beef) to inhibit the growth of *Clostridium botulinum* (the bacterium that produces *botulinum toxin*) and to prevent red meats from turning brown. (Food poisoning by *botulinum toxin* is often fatal.) In the presence of acid or under the influence of heat, sodium nitrite reacts with amines which are always present in the meat to produce *N*-nitrosamines. Cooked bacon, for example, has been shown to contain *N*-nitrosodimethylamine and *N*-nitrosopyrrolidine.

However, nitrites (and nitrates that can be converted to nitrites by bacteria) which occur naturally in many foods may produce nitrosamines when they react with amines in the presence of the acid found in the stomach but, researchers revealed that due to protective effects of nutrients such as vitamin C in vegetables inhibit the formation of toxic nitrosamines. Thus, manufacturers of processed meat are instructed to add antioxidant vitamin C or vitamin E while processing of meat. Also, FDA reduced the permissible amount of nitrites allowed in cured meats from 200 parts per million (ppm) to 50–125 ppm.



CROSSWORD



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ACROSS

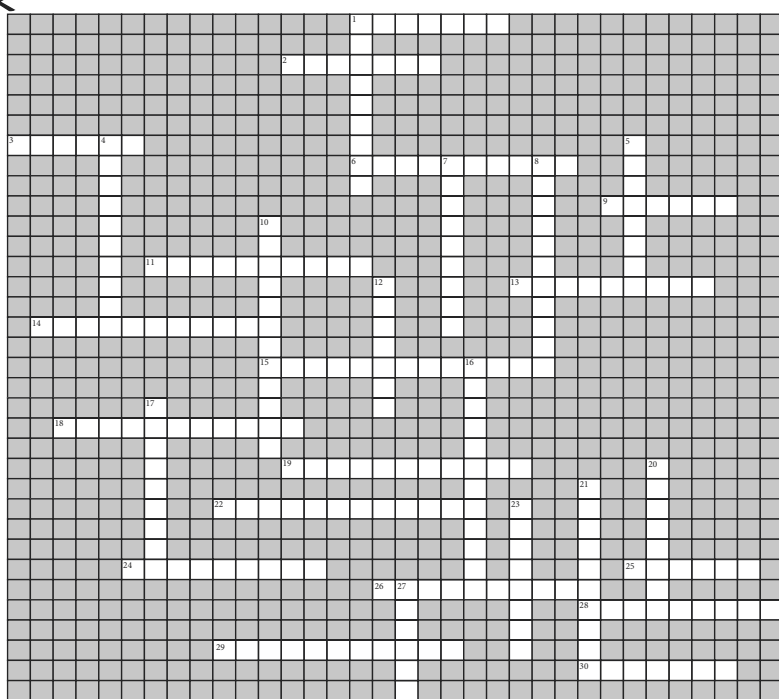
1. Measure of lifting capacity of hot air. (7)
2. Substance formed when acetylene combines with ammonia at high temperature. (7)
3. Purest variety of silica. (6)
6. Reagents having electron attracting and electron repelling sites. (10)
9. Metal present in vitamin B₁₂. (6)
11. Bursting of RBCs when placed in pure water. (10)
13. An organometallic species that reacts like a carbene. (9)
14. Glassy mass formed on first heating sucrose slowly and then cooling it. (11)
15. Another name for oxoprocess. (13)
18. A highly branched polymer of α -D-glucose units. (11)
19. Elements which combine primarily with oxygen and are most abundant in earth crust. (11)
22. Nuclei having only one stable isotope. (12)
24. The term catalysis was coined by _____. (9)
25. Series of spectral lines of hydrogen atom which lie in the visible region. (6)
26. A hypnotic drug. (10)
28. An indicator used for the titration involving weak acid and weak base. (9)
29. A sulphide ore of iron and nickel. (11)
30. A smokeless explosive obtained by mixing glyceryl trinitrate with gun cotton and vaseline. (7)

DOWN

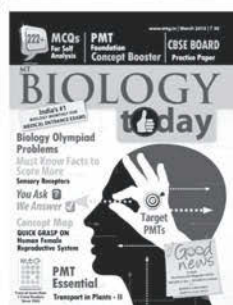
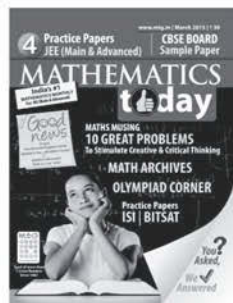
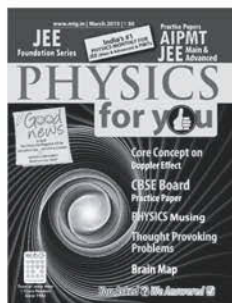
1. Geometry of F₂SeO. (9)
4. Crystal system having five planes of symmetry and five axes of symmetry. (10)
5. Product of dehydration of glycerol with KHSO₄. (8)
7. Binary compounds of group 15 elements. (9)

8. Name of H₉O₄⁺ ion. (11)
10. An acid which exists as a white solid containing octahedral Te(OH)₆ molecules. (12)
12. Another name of isotope ²¹⁹Rn. (7)
16. Reactions having molecularity equal to three. (12)
17. A polymer which forms water resistant and quick drying fibre. (9)
20. A synthetic organic compound used as anaesthetic in dentistry. (8)
21. Carbonyl compounds containing metal and CO only. (10)
23. The process in which particles of dispersed phase unites to form thread like chains which become semisolid and particles of dispersion medium get trapped in the cavities of these chains. (8)
27. Substance having lowest boiling point. (6)

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